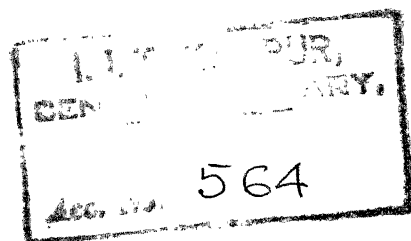


Vapor-Liquid Equilibrium Data for Methanol Methyl Chloride System at 550 mm. and for Toluene Benzal- Dehyde System at 760 mm. Mercury Pressure

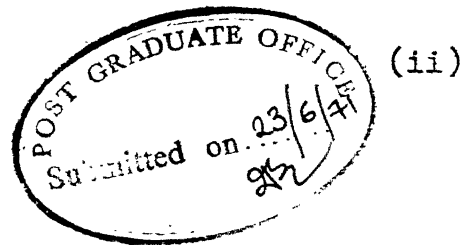
A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of
MASTER OF TECHNOLOGY



BY
SANTANU KUMAR CHHOTRAY

to the

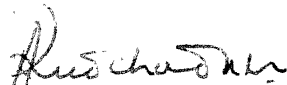
DEPARTMENT OF CHEMICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY KANPUR
MAY 1971




CERTIFICATE

It is certified that this work has been carried out under my supervision and that this has not been submitted elsewhere for a degree.

Date: 25th May 1971


Arvind P. Kudchadker
Assistant Professor of
Chemical Engineering
Indian Institute of Technology
Kanpur, India

POST GRADUATE OFFICE
This thesis has been approved
for the award of the Degree of
Master of Technology (M.Tech.)
in accordance with the
regulations of the Indian
Institute of Technology Kanpur
Date 9.9.71 

ACKNOWLEDGEMENTS

The author expresses his deep gratitude to Dr. Arvind P. Kudchadker, for his guidance, his advice and suggestions, his criticisms, and his words and acts of encouragement.

Thanks are due to Mr. R.A. Thakur for his ready help in all the glass blowing works.

The author is thankful to Mr. B.S. Pandey and Mr. R.P. Gupta for typing the manuscript.

The financial aid from the Kanpur Critical Data Center is gratefully acknowledged.

Author

TABLE OF CONTENTS

			PAGE
	ACKNOWLEDGEMENT	...	(iii)
	ABSTRACT	...	ix
I	INTRODUCTION	...	1
II	REVIEW OF PAST WORK REGARDING THE EQUILIBRIUM STILL	...	4
III	THEORY OF VAPOR-LIQUID EQUILIBRIUM	...	6
IV	EXPERIMENTAL SET-UP	...	17
	Equilibrium Still	...	17
	Condenser	...	23
	Manometer	...	24
	Ebulliometer	...	24
	Other Accessories	...	28
V	EXPERIMENTAL PROCEDURE	...	30
	Sample Purity	...	30
	Feeding of Sample into equilibrium still	...	32
	Maintenance and Measurement of pressure	...	33
	Measurement of Equilibrium Temperature	...	35
	Operation of the still	...	36
	Withdrawal of Equilibrium Sample	...	38
	Analysis of Equilibrium Samples	...	43
VI	EXPERIMENTAL RESULTS	...	45
VII	CALCULATION OF DERIVED THERMODYNAMIC PROPERTIES	...	58

VIII	THERMODYNAMIC CONSISTENCY TESTS	...	72
IX	DISCUSSION OF RESULTS	...	80
X	SUGGESTIONS FOR FUTURE WORK	...	83
	Equilibrium Still	...	83
	Heating device in the still	...	84
	NOMENCLATURE	...	x
	LITERATURE CITED	...	85
APPENDICES			
1	Properties of Pure Compounds	...	88
2	Calibration of Thermocouples	...	89
3	Calibration of Refractometer	...	90
4 (a)	Molar Volumes as function of temperatures for methanol	...	94
(b)	Virial Coefficients as function of temperature for methanol and methylene chloride	...	94
(aG)	Virial Coefficients and Molar Volumes for Toluene and Benzaldehyde	...	92

LIST OF TABLES

TABLE		PAGE
1	Physical Properties of the Pure Substances	31
2	Experimental Data for Methanol-methylene Chloride System at 550 mm Hg. Pressure.	46
3	Experimental Data for Toluene Benzaldehyde System at 760 mm Hg. Pressure.	49
4	Experimental t-x-y data for methanol-methylene chloride system at 550 mm Hg. pressure	51
5	Experimental data for toluene benzaldehyde system at 760 mm Hg. pressure	53
6	Smoothed t-x-y data for methanol-methylene chloride system at 550 mm Hg. Pressure	55
7	Smoothed t-x-y data for toluene-benzaldehyde system at 760 mm Hg. pressure	56
8	Activity Coefficients for Methanol and Methylene Chloride at 550 mm Hg. pressure	61
9	Activity coefficients of toluene and Benzaldehyde at 760 mm Hg. pressure.	63
10	Relative Volatility and K values for methanol and methylene chloride at 550 mm Hg. pressure	65
11	Relative volatility and K values for toluene and Benzaldehyde at 760 mm Hg. pressure.	67

...

LIST OF ILLUSTRATIONS

FIGURE		PAGE
1.	Temperature-Composition Diagram of Extremum Azeotropes at Constant Pressure	14
2.	Equilibrium Still	21
3.	Single Stage Swietoslawsky Ebulliometer	25
4.	Schematic Line Diagram of the Experimental Set up	26
5.	Temperature Measuring Circuit	34
6.	Thermocouple Calibration Circuit with Platinum Resistance Thermometer.	37
7.	Calibration of Thermocouples	39
8.	Calibration of Refractometer	
	a) Methanol-methylene chloride system	41
	b) Toluene-benzaldehyde System	42
9.	Experimental Temperature (t) - composition (x,y) diagram for methanol-methylene chloride system at 550 mm. Hg. pressure.	47
10.	Experimental temperature (t) - composition (x,y) diagram for toluene-benzaldehyde system at 760 mm. Hg. pressure.	50
11.	x-y diagram for methanol methylene chloride system at 550 mm. Hg. pressure	52
12.	x-y diagram for toluene-benzaldehyde system at 760 mm. Hg. pressure.	54
13.	Activity Coefficient-composition (x_1) diagram for methanol-methylene chloride system at 550 mm Hg. pressure.	62
14.	Activity coefficient-composition (x_1) diagram for toluene-benzaldehyde system at 760 mm. Hg. pressure.	64

15	Relative Volatility Composition (x_1) diagram for methanol-methylene chloride system at 550 mm. Hg. pressure	66
16	Relative Volatility-Composition (x_1) diagram for toluene-benzaldehyde system at 760 mm. Hg. Pressure	
17	Log γ_1/γ_2 vs x_1 diagram for methanol- methylene chloride system at 550 mm Hg. Pressure	77
18	Log γ_1/γ_2 vs x_1 diagram for toluene- benzaldehyde system at 760 mm. Hg. Pressure	78

ABSTRACT

Isobaric vapor-liquid equilibrium data for methanol-methylene chloride system at 550 mm.Hg. and for Toluene-Benzaldehyde system at 760 mm Hg. pressure were investigated in an improved vapor recirculating still. The former was found to exhibit a minimum boiling azeotrope at 28.88°C and 88.5 mole percent methylene chloride at 550 mm.Hg. pressure. For the latter the nature of the t-x-y and x-y curves indicated that the required separation could be affected with ease. The binary mixtures were analysed by refractive index measurements. The pressure was accurately measured by a Swietoslawskyebulliometer. The activity coefficients were calculated by considering the vapor-phase non-ideality and it was observed that the activity coefficient versus liquid composition exhibited a maxima for the methanol-methylene chloride system at a fairly dilute concentration range of the more volatile component thus indicating the highly non-ideal behavior of the components in both the phases.

Experimental data for the methanol-methylene chloride system were found to be consistent with Herrington's area test and the data were well fitted with the third order α equation (where α is the relative volatility), proposed by Hala et.al. The standard models i.e. Wilson, 3-suffix Margules, etc. failed to represent the activity coefficients composition data.

For the toluene-benzaldehyde system the ^{Herrington area test}~~Gibbs-Duhem~~ Equation is satisfied.

NOMENCLATURE

A	Constant of the Antoine equation
$a_{12},$ $a_{122},$ $a_{21},$ a_{211}	Constants of the third order α -equation.
B	Constant of the Antoine equation
B_{ij}	Cross virial coefficient of components i and j
C	Constant of the Antoine equation
$^{\circ}\text{C}$	Degree Celcius
f	Fugacity
G	Gibbs energy
ΔG	Change in Gibbs energy
H	Enthalpy
Hg	Mercury
i	Species 'i'
j	Species 'j'
K	Separation Factor
L	Liquid phase
m	Number of components
n_T	Total number of moles
n_D	Refractive Index
P_c	Critical Pressure
P_s	Saturated vapor pressure
p	Partial pressure

P	Total pressure
P_r	Reduced pressure
R	Gas constant
S	Entropy
T	Absolute temperature
T_c	Critical Temperature
t	Celcius temperature
U	Internal Energy
V	Total volume
V_c	Critical volume
v	Molar volume
x	liquid phase mole fraction
y	Vapor phase mole fraction
Z	Compressibility factor
Z_c	Critical compressibility factor
α	Relative volatility
β	Phase index
γ	Activity coefficient
f	Fugacity coefficient
π	Total number of phases
μ	Chemical potential
ω	Acentric factor
Σ	Summation sign

CHAPTER 1

INTRODUCTION

A knowledge of the phase equilibrium properties is frequently required in chemical engineering plant operations. One everyday use of such information is the calculation of the performance of the plant in which mass transfer between phases takes place. Common examples of such plants are the distillation column, absorption tower, cooling towers etc.

There are relatively few systems whose equilibrium relations can be calculated from Raoult's law and Dalton's law of partial pressure. On the other hand, there are a large number of infinitely important systems whose equilibrium relations cannot be predicted from purely theoretical considerations and hence must be obtained by experimental determinations. The determination of equilibrium curves can be carried out either at constant pressure or at constant temperature. For distillation calculations, the isobaric data are frequently used. Hence, an attempt is made here to investigate the isobaric vapor liquid equilibrium data for a couple of binary mixtures of both theoretical and industrial importance.

The methanol-methylene chloride ($\text{CH}_3\text{OH}-\text{CH}_2\text{Cl}_2$) system is theoretically important because of the associative nature of both the components ($\mu_{\text{CH}_3\text{OH}} = 1.71$ debye and $\mu_{\text{CH}_2\text{Cl}_2} = 1.54$)

3. The investigation of the system at 550 mm.Hg. pressure

was of particular interest to the Hindustan Photo Films, Ootacamund. Besides, it is quite interesting to study this system since the data for methanol with chloromethanes like chloroform and carbontetrachloride have already been reported. (41) Toluene-benzaldehyde system ($C_6H_5-CH_3-C_6H_5-CHO$) was chosen as part of the investigation for the prediction of vapor liquid equilibria at 760 mm Hg pressure of a five component mixture, i.e. Toluene-Benzaldehyde-Benzyl alcohol-Benzyl benzoate-Benzoic acid from the binary data by the Prausnitz's method. No vapor liquid equilibrium data are available in the literature for this system.

The purpose of the present investigation was the following:

1. Experimental determination of the vapor-liquid equilibrium data for $CH_3OH-CH_2Cl_2$ system at 550 mm.Hg pressure.
2. To study the effect of pressure on the azeotropic point of the above system using the data at 750 and 760 mm Hg. pressure of Tenn and Missen (41) and of Sarma (36) respectively.
3. Experimental determination of the vapor-liquid equilibrium data for toluene-benzaldehyde system at 760 mm.Hg. pressure.
4. Computations of the activity coefficients and the excess functions for both the systems.
5. To present the data by a model such as, the three-suffix Margules equation, Wilson equation, third order -equation, etc.

Chapter 2 deals with a brief description of the past work carried out in developing the equilibrium still used in the present investigation.

Chapter 3 deals with the basic principles and theories behind the vapor liquid equilibria for real solutions and the procedure for calculating the various thermodynamic properties from the experimental data.

Chapter 4 deals with the design of the experimental set-up used in this investigation. It gives a detailed description of the equilibrium still, its construction and operation along with the description of all the important accessories.

Chapter 5 briefly describes the experimental procedure in measuring the equilibrium temperatures and compositions.

Chapter 6 tabulates all the measured experimental results and Chapter 7 consists of all the derived thermodynamic properties calculated from the observed experimental results.

Chapter 8 outlines the procedure for testing the thermodynamic consistency of the data and clearly describes the various models which were tried to fit the experimental data.

Chapters 9 and 10 conclude the work with a critical discussion of the results, and the suggestions for future work.

#

CHAPTER 2

REVIEW OF PAST WORK REGARDING THE EQUILIBRIUM STILL

A complete literature survey indicates that although the work in this area started since 1913 by Jamaguchi (1^r) and Shamashima (23), practically Othmer (27) was the pioneer in developing an equilibrium still which could give satisfactory results. Over the years the Othmer still has gone through various modifications. Based on the modified Othmer still, Hipkin and Myers designed a vapor recirculating still lagged by its own vapor and obtained the vapor liquid equilibrium data for Heptane-Toluene system and the methanol-carbontetrachloride system. They have used the still extensively to obtain the equilibrium data for paraffin with aromatics(24). Almost all the investigations were carried out at atmospheric and subatmospheric pressures. The Hipkin and Myers' apparatus was further used by Sinor and Weber (38) to determine the equilibrium data of ethyl alcohol with n-hexane, methylcyclopentane etc. over a range of 180 mm to 760 mm.Hg. pressure. Yen and Reed (46) modified the Hipkin and Myers' still in 1959 to study some fluoro carbon systems of parafluoroheptane with perfluoro cyclic oxides. Some modifications were also made by Ita and Yoshider (49) and the data for water formic acid system and water-acetic acid system at 700, 200 and 70 mm.Hg. pressure were investigated. Recently in 1967, Lodl and

Scheller (36) further modified the Hipkin and Myers still and obtained the isothermal data for n-haptane-n-valeric acid system at 50°, 75° and 100°C. In 1970 ~~Sarma~~ (35) used the Hipkin and Myers still as modified by Lodl and Scheller to carry out the vapor liquid equilibrium studies of $\text{CH}_3\text{OH}-\text{CH}_2\text{Cl}_2$ system at 760 mm Hg. pressure. In 1963, this system was investigated by Tenn and Missen (40).

In the present work the vapor liquid equilibrium data for the methanol-methylenechloride system at 550 mm and toluene-bezaldehyde system at 760 mm.Hg. pressure was investigated with the still of Lodl and Scheller design (36) with some modifications in the still and the condenser assembly. The condenser design was completely changed to facilitate condensation of vapors, the contactor was provided with some additional slots to help in better contact of the vapor with the liquid, and the heater well dimensions were reduced to affect a controlled heat input to avoid bumping. The heater well was provided with protrusions all along the surface to facilitate smooth boiling of the liquid in the vaporizer.

#

CHAPTER 3

THEORY OF VAPOR LIQUID EQUILIBRIA

A homogeneous system is one with **uniform** properties throughout (31); that is a property which has the same value from point to point in a macroscopic sense. A phase is a homogeneous system. A closed system is one which does not exchange matter with the surroundings, although it may exchange energy. A heterogeneous closed system is made up of two or more phases with each phase considered as an open system within the overall closed system. An equilibrium state is one from which there is no tendency to depart spontaneously having in mind some permissible changes or processes, such as , (i) heat transfer, (ii) work or volume displacement, and (iii) mass transfer across a phase boundary. In an equilibrium state, values of the properties are independent of time and of the previous history of the system; further, they are stable, that is, not subject to catastrophic changes on slight variations of external conditions.

An attempt is made here to find out the conditions under which the heterogeneous system is in a state of internal equilibrium with respect to the three processes of heat transfer, boundary displacement, and mass transfer.

Let us consider a function 'U' to show that the temperature, pressure and the chemical potential of each

species must be uniform throughout a closed heterogeneous system at equilibrium with respect to the three processes mentioned above. Since an equilibrium process is identified with reversible processes, the criterion for equilibrium in a closed system is that the property 'U' is minimum, and that any variation in 'U' at constant total entropy and total volume vanishes; that is $dU_{S,V} = 0$. If β denotes the phase index and i the species index, the expression for dU for all the phases and for all the components present may be written as follows (by combining the first and the second law of thermodynamics.)

$$dU = \sum_{\beta} T^{(\beta)} ds^{(\beta)} - \sum_{\beta} P^{(\beta)} dv^{(\beta)} + \sum_{\beta} \sum_i \mu_i^{(\beta)} dn_i^{(\beta)} \quad (1)$$

If there are π phases and 'm' components; expansion of Equation 1 gives

$$\begin{aligned} dU = & T^{(1)} ds^{(1)} - P^{(1)} dv^{(1)} + \mu_1^{(1)} dn_1^{(1)} + \dots + \mu_m^{(1)} dn_m^{(1)} \\ & + T^{(2)} ds^{(2)} - P^{(2)} dv^{(2)} + \mu_1^{(2)} dn_1^{(2)} + \dots + \mu_m^{(2)} dn_m^{(2)} \\ & \vdots \\ & + T^{(\pi)} ds^{(\pi)} - P^{(\pi)} dv^{(\pi)} + \mu_1^{(\pi)} dn_1^{(\pi)} + \dots + \mu_m^{(\pi)} dn_m^{(\pi)} \end{aligned} \quad (2)$$

The individual variations $ds^{(1)}$, etc. are subjected to the constraints of constant total entropy, constant total volume and constant total moles of each species (under going no chemical reaction).

$$\therefore ds = ds^{(1)} + ds^{(2)} + \dots + ds^{(\pi)} = 0 \quad (3)$$

$$dv = dv^{(1)} + dv^{(2)} + \dots + dv^{(\pi)} = 0 \quad (\text{For } \pi \text{ Phases}) \quad (4)$$

$$\text{and } \sum_{\beta} dn^{(\beta)} = dn_1^{(1)} + \dots + dn_i^{(\pi)} = 0 \quad (5)$$

By eliminating $ds^{(1)}$, $dv^{(1)}$ and $dn_1^{(1)}$ from Eqn.(2) with the help of Equations 3, 4 and 5, we obtain

$$\begin{aligned} du = & (T^{(2)} - T^{(1)}) ds^{(2)} - (P^{(2)} - P^{(1)}) dv^{(2)} \\ & + (\mu_1^{(2)} - \mu_1^{(1)}) dn_1^{(2)} + \dots + (\mu_m^{(2)} - \mu_m^{(1)}) dn_m^{(2)} \\ & + \dots + \dots + \dots \\ & + (T^{(\pi)} - T^{(1)}) ds^{(\pi)} - (P^{(\pi)} - P^{(1)}) dv^{(\pi)} \\ & + (\mu_1^{(\pi)} - \mu_1^{(1)}) dn_1^{(\pi)} + \dots + (\mu_m^{(\pi)} - \mu_m^{(1)}) dn_m^{(\pi)} \quad (6) \end{aligned}$$

All variations

$$\begin{aligned} & dS^{(1)} \\ & dV^{(1)} \\ & \text{and } dn_2^{(2)} \quad \quad \quad dn_2^{(1)} \quad \text{etc.} \\ & \quad \quad \quad (i=1, m) \end{aligned}$$

truly independent.

Hence at equilibrium in a closed system where $dU=0$; we have,

$$\frac{\partial U}{\partial S^{(1)}} = 0, \quad \dots \quad \frac{\partial U}{\partial S^{(m)}} = 0 \quad (7)$$

$$\frac{\partial U}{\partial V^{(2)}} = 0, \quad \dots \quad \frac{\partial U}{\partial V^{(2)}} = 0 \quad (8)$$

and $\frac{\partial U}{\partial n_2^{(1)}} = 0, \quad \dots \quad \frac{\partial U}{\partial n_2^{(m)}} = 0 \quad (9)$

Hence for a binary mixture with two phases

$$T^{(2)} = T^{(1)} = 0 \quad (10)$$

$$p^{(2)} = p^{(1)} = 0 \quad (11)$$

and

$$\mu^{(2)} = \mu^{(1)} = 0 \quad (12)$$

$$T^{(2)} = T^{(1)} \quad (13)$$

$$p^{(2)} = p^{(1)} \quad (14)$$

$$\mu_1^{(1)} = \mu_1^{(2)} \quad \text{and} \quad \mu_2^{(1)} = \mu_2^{(2)} \quad (15)$$

Equations 13, 14 and 15 represent the internal equilibrium with respect to the above three processes. Thus it is established that a liquid phase and a vapor phase are in thermodynamic equilibrium when the temperature pressure of each phase is equal to that of the other and when the chemical potential of each molecular species present is the same in both phases (32).

Thus for two phases which are at the same temperature, the equation of equilibrium for each component 'i' is expressed in terms of the fugacity ' f_i '.

$$f_i^v = f_i^l \quad (16)$$

where v and l represent the vapor and liquid phases respectively.

The fugacities can be related to the experimentally accessible quantities like x, y, T and P where x stands for the liquid phase mole fraction, y for vapor phase mole fraction, T for the absolute temperature, and P for the total pressure which is same for both the phases. (Isobaric operation)

The simplified relation between fugacities and experimentally accessible quantities is obtained through some auxiliary functions which are defined as fugacity coefficients

(ϕ) and activity coefficients (γ_i) and they account for the vapor phase and liquid phase non-idealities respectively.

$$\Phi = f_i^V / P y_i \quad (17)$$

and
$$\gamma_i = f_i^L / x_i f_i^{OL} \quad (18)$$

where f_i is the standard state fugacity.

Combining Equations 16, 17 and 18, we obtain

$$\Phi_i P y_i = \gamma_i x_i f_i^{OL} \quad (19)$$

The expression for ϕ_i is given by Beattie ~~is~~ is,

$$\ln \Phi_i = \frac{1}{RT} \int_v^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, v, n_j} - \frac{RT}{v} \right] dv - \ln Z \quad (20)$$

$j \neq i$

where Z is the compressibility factor given by (20)

$Z = \frac{PV}{nRT}$ for the mixture. Thus to obtain numerical results for activity coefficients it is necessary to substitute a particular equation of state into Equation (20). At low and moderate pressures the virial equation of state truncated to the second virial coefficient is usually satisfactory.

The truncated virial equation of state is,

$$Z = \frac{Pv}{RT} = 1 + \frac{Bv(T)}{v} \quad (21)$$

For a mixture (since practically it is only the mixtures that are dealt with)

$$B_{mix} = \sum_{i=1}^N \sum_{j=1}^N y_i y_j B_{ij} \quad (22)$$

For a binary mixture

$$B_{mix} = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}$$

In general B_{ij} depends only on the temperature and on the species i and j . combining Equations (20, 21 and 22 fugacity coefficient for component i in the mixture is obtained.

$$\text{Now } B_{ij} = (B_{ii} B_{jj})^{1/2} \quad (23)$$

and Z for the mixture is given by $Z = \frac{p_0}{RT}$

$$\therefore \ln \Phi_i = \frac{2}{v_{mix}} \left(\sum_{j=1}^N y_j B_{ij} \right) - \ln Z_{mix} \quad (24)$$

For pure non-polar gases, B_{ii} maybe calculated by Pitzer's expression (31), if no experimental data are available.

$$\begin{aligned} \frac{P_i B_{ii}}{RT_c} &= (0.1445 + 0.073 w) \\ &\quad - (0.330 - 0.46 w) \text{Tr}^{-1} \\ &\quad - (0.1385 + 0.50 w) \text{Tr}^{-2} \\ &\quad - (0.0121 + 0.09 w) \text{Tr}^{-3} \\ &\quad - (0.0073 w) \text{Tr}^{-8} \end{aligned} \quad (25)$$

ω = Acentric factor

$$= -\log_{10} Pr - 1.0 \quad (\text{at } Tr=0.7) \quad (26)$$

In the case of polar gases, Eqn.(25) is extended by adding one more term which is a function of the dipole moment (33).

The reference state fugacity coefficient is given by

$$f_i^{OL} = \Phi_i^s P_i^s$$

where Φ_i^s is the fugacity coefficient of pure vapor i at temperature T and saturation pressure P_i^s and is given by

$$\ln \Phi_i^s = \frac{2}{\rho_i^s} B_{ii} - \ln z_i^s \quad (28)$$

$$\text{with } z_i^s = P_i^s v_i^s / RT = 1 + \frac{B_{ii} P_i^s}{v_i^s} \quad (29)$$

Thus the reference state fugacity i.e. the fugacity of pure liquid i at temperature T and at a reference pressure chosen to be zero is given by

$$f_i^{OL} = P_i^s \Phi_i^s \exp \left(- \frac{v_i^L P_i^s}{RT} \right) \quad (30)$$

This set of equations completely establishes the theory behind the general calculation procedure of the vapor liquid equilibria.

Azeotropes:

In the field of vapor liquid equilibrium, and in its practical application to distillation problems, the phenomena of azeotrope formation occupies an important and unique

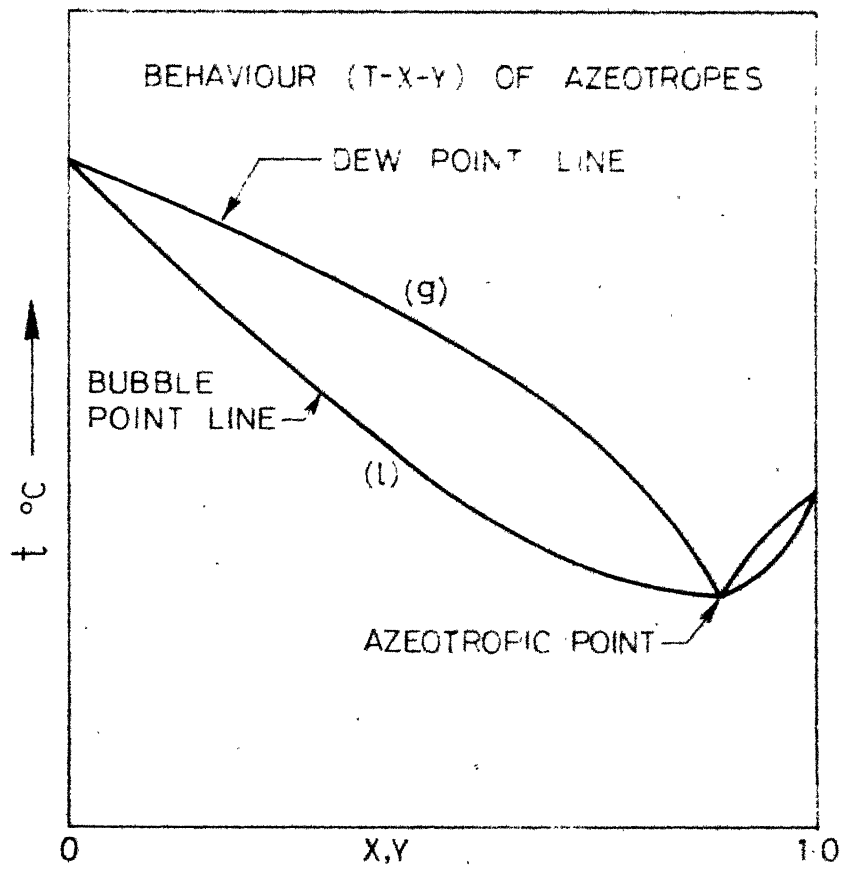


FIG. 1a. MINIMUM BOILING AZEOTROPE

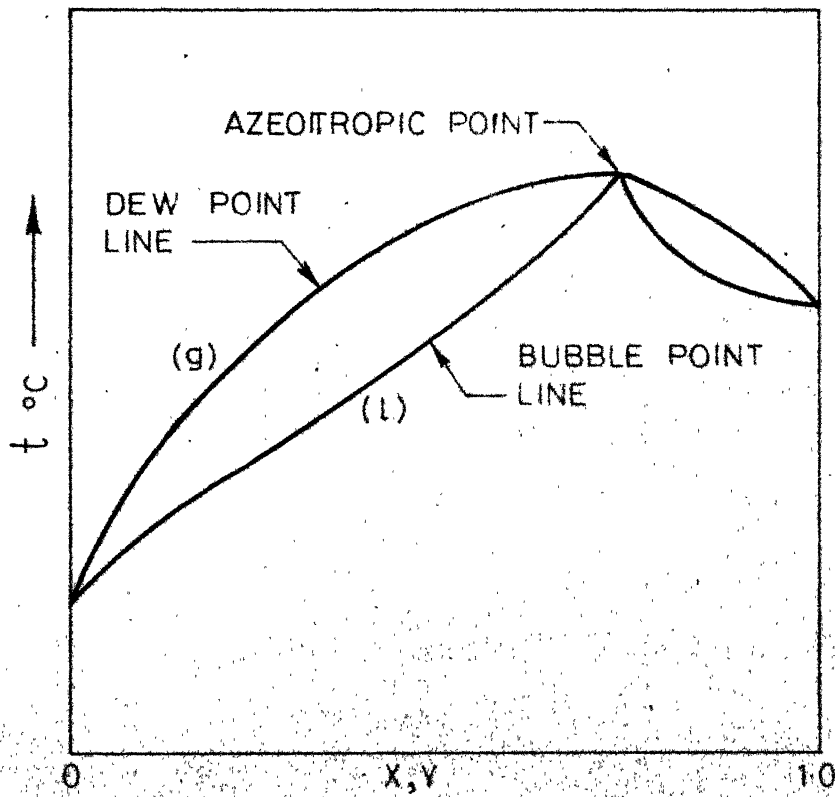
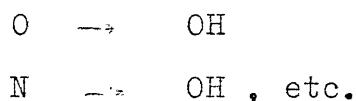


FIG. 1b. MAXIMUM BOILING AZEOTROPE

position. Azeotropy is the term applied to distillation or rectifications (6) which involve the formation of constant boiling mixtures. An azeotrope is one where the composition of the more volatile component becomes same in both the liquid and the vapor phases at the same temperature. The formation of constant boiling mixtures is a function of the difference in temperature between the two components and the non-ideality of the resulting solution. Since the formation of constant boiling mixtures is a function of the non-ideality of the mixture, the ideal behavior of the solutions can seldom be expected in such cases. Formation of azeotropes may be attributed to the effects of hydrogen bonds or internal pressure, of which the former is the more important. The concept of hydrogen bonds is that hydrogen can co-ordinate between two molecules of oxygen, nitrogen etc. The strength of hydrogen bonds depends upon the nature of the atoms between which the hydrogen is coordinating. There exists a strong coordination bond between



The azeotropes can be either minimum boiling or maximum boiling depending upon whether the boiling points of both the pure components are either less or greater the azeotropic temperature respectively. This is shown as follows (8) in Figures 1(a) and 1(b).

$\text{CH}_3\text{OH} - \text{CH}_2\text{Cl}_2$ system forms a minimum boiling
ageotrope and the calculation procedure for this system
is exactly the same as described above.

#

CHAPTER 4

EXPERIMENTAL SET-UP

The experimental set up designed for the investigation of the vapor-liquid equilibrium data for the above systems consist of the following main components.

1. Equilibrium cell,
2. Condenser,
3. Manometer,
4. Ebulliometer,

A detailed description of the individual components is given here so far their construction and operation is concerned.

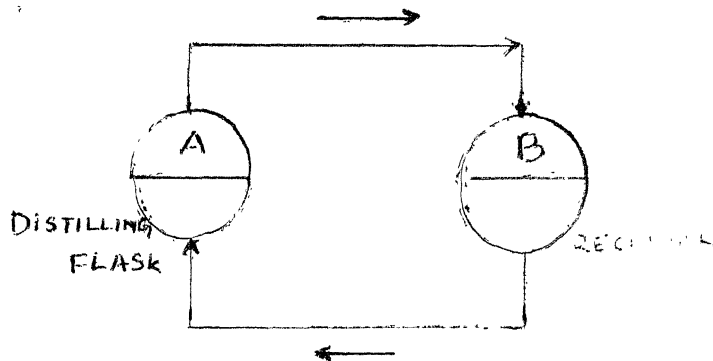
The Equilibrium Cell:

The equilibrium cell used in this investigation is a vapor-recirculation type with its own vapor acting as a lagging jacket to prevent heat loss and hence to maintain an adiabatic atmosphere. This type of a cell can be used at both the high and low pressures and has found considerable use in many experimental investigations as described in Chapter 2.

Principle:

Even though there are various equilibrium cells which are different in construction, the common principle (10) behind their operation is same and is as follows. The vapors evolved from the boiling mixture in the distilling

flask (A) pass through the vapor conduit (\rightarrow) and after condensation collect in the receiver (B). After filling the



the receiver the condensate returns to (A) through the liquid conduit (\leftarrow). This process continues until the steady state is attained, in which the compositions in both the vessels no longer change with time.

$$\text{i.e.} \quad \frac{dx_A}{dt} = \frac{dx_B}{dt} = 0 \quad (32)$$

x_A and x_B represent the composition of the more volatile component in vessels A and B at steady state. If the distillation occurs with a finite velocity, then during the interval 'dt', dn moles of mixture pass from A to B and in the same period dn moles return in the reflux to the flask from B to A.

$$\frac{\overset{\rightarrow}{dn}}{dt} = \frac{\overset{\leftarrow}{dn}}{dt}$$

If the vapor evolved above the mixture of composition \vec{x}_A is \vec{y}_A , then the amount of volatile component transferred from A to B is $\vec{y}_A \overset{\rightarrow}{dn}$ and the amount of this constituent

transferred from B to A is $(x_B \leftarrow dn)$,

Thus by a material balance on the more volatile component;

$$y_A \xrightarrow{\quad} dn = x_B \xleftarrow{\quad} dn \quad (33)$$

Combining (32)&(33) $y_A \xrightarrow{\quad} \frac{dn}{dt} - x_B \xrightarrow{\quad} \frac{dn}{dt} = 0 \quad (34)$

or $(y_A - x_B) \xrightarrow{\quad} \frac{dn}{dt} = 0 \quad (35)$

since for finite velocity of distillation;

$$\begin{aligned} \xrightarrow{\quad} \frac{dn}{dt} \neq 0 \quad y_A - x_B &= 0 \\ x_B &= y_A \end{aligned}$$

This establishes the fact that the liquid composition in the liquid sample bottle is equal to the vapor composition in the boiling mixture from the distillation flask on the assumption of equilibrium between the liquid phase and the evolved vapor phase.

Hence the "Steady State corresponds to phase equilibrium".

The basic principle underlying this equilibrium cell is exactly the same excepting a slightly different flow path for the liquid and the vapor. This may be schematically represented in Figure .

Feed is charged at two different points as shown in Figure above and requisite amount of voltage is supplied to the heater to vaporize the mixture (or pure component, as the case may be) and the vapor thus produced is allowed to

bubble through the slots made in the contactor and vaporize the mixture which generates vapor which condenses in the condenser and mixes the liquid in the vaporizer and thus completes the cycle. This cycle goes on till the vapor and liquid are in equilibrium with each other thus reaching a steady state and hence there is no further mass transfer from any of the phases with time.

The modified design of the Hipkin and Mayer still (12) proposed by Lodl and Sheller (36) is shown in Figure . The still is designed so that the contactor is self lagged with its own vapor. This ensures adiabatic operation (no heat flow to or from the apparatus) and thus eliminates additional equipment necessary to maintain adiabatic conditions. Besides, this is a compact unit isolated from the rest of the experimental set up which thus enables easy handling.

Construction of the Equilibrium Cell:

The whole apparatus is made up of glass (pyrex) to stand a pressure as high as 3-4 atms. and a temperature as high as 500°C. This contains a vacuum jacket which is silvered which thus helps in preventing heat loss by radiation. Next to the vacuum jacket is the vaporizer of 40 cc capacity which otherwise is known as the boiler. This contains the liquid mixture (or the pure liquid as the case may be) to be heated. The next component is the contactor

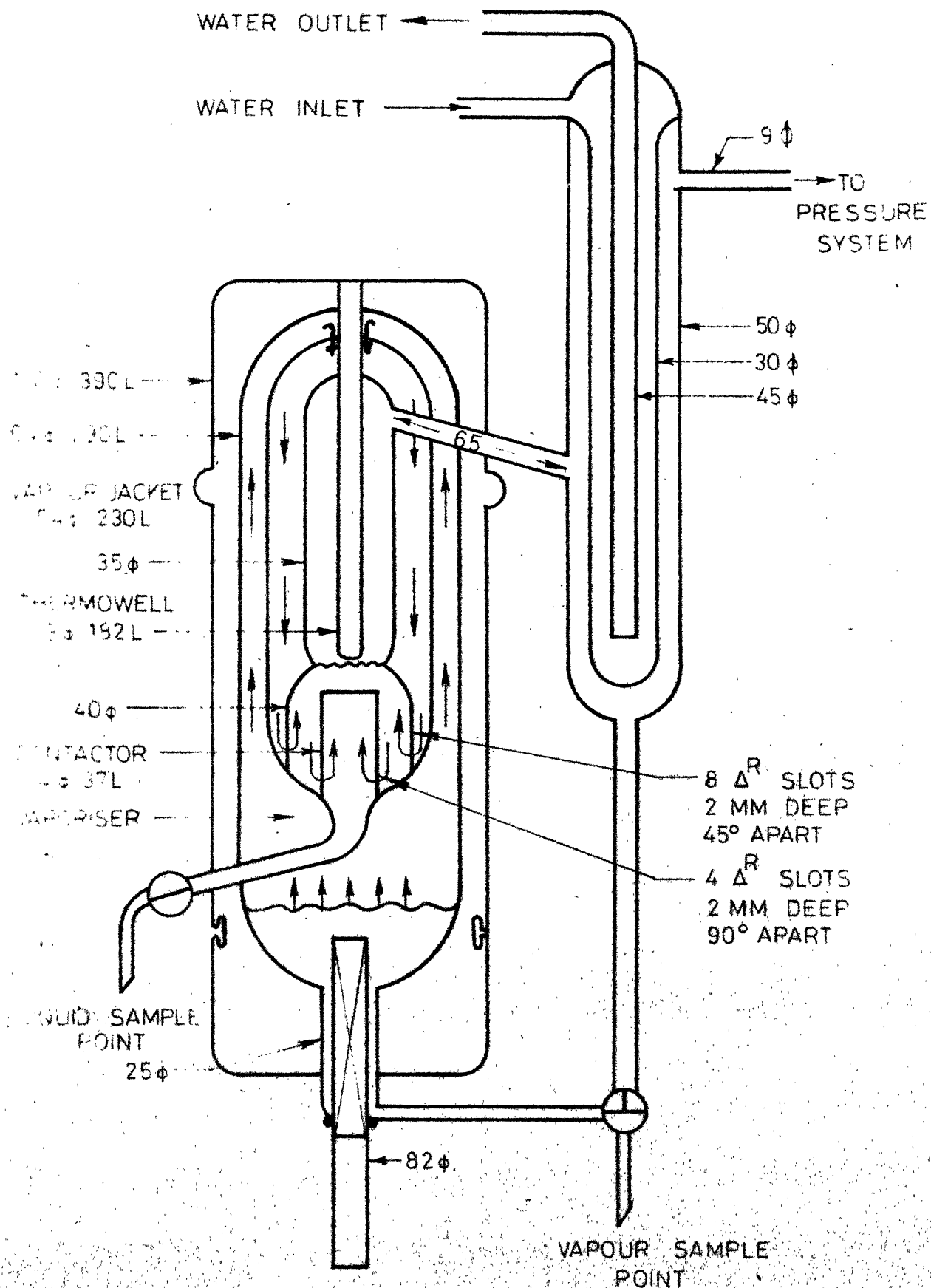


FIG 2 EQUILIBRIUM CELL AND CONDENSER ASSEMBLY
(ALL DIMENSIONS IN MM.)

(separated by a wall from the vaporizer) which is of 50 cc capacity with 8 triangular slots, 2 mm deep and are separated at an angle of 45 degrees. The slots are made to allow the incoming vapor from the vaporizer to bubble through the liquid in the contactor and hence to allow the vapor and the liquid to come in intimate contact with each other. This also contains a tube known as the contactor tube which is open at both the ends with one end opening to the outside by means of a tubing to allow feed to be charged in the contactor. Four triangular slots of 2mm deep separated by an angle of 90° are made in the contactor tube to ensure more contact of the vapor with the liquid and to allow all the liquid in the contactor to be completely removed with ease when necessary. This section also contains a thermo-well which extends right upto the contactor from the top and opens to the outside. The still is silvered with a 0.5 inch viewing strip.

The Heater: The heater forms an integral part of the equilibrium cell. This heater design is flexible and is designed depending upon the temperature range required to boil the liquid in the vaporizer. The heater is usually made up of Nichrome wire (24 gauge, with resistance 7.8 ohms/meter length) wound on the glass tube which is wrapped with asbestos cloth. Heat input to the heater is controlled by controlling the voltage through a variac.

Sample Valves:

The equilibrium cell used in the Hipkin and ~~Myers~~ work and also in Lodl and Scheller's work made use of Teflon stop-cocks. For this work also, teflon stop cocks were designed and fabricated but they could not be found satisfactory because of the following two reasons; (1) they could not withstand high vacuum and (2) they were too heavy to be used in the glass lines. Besides, the cost of material and labor put in fabricating them is enormously high compared to high vacuum stop-cocks which serve the purpose quite efficiently. Hence ultimately glass stop-cocks of 4 mm bore (Corning, and Ace Glass stop-cocks made in U.S.A.) were used in liquid circulating line with the still.

The still is connected to the condenser with a slanted tube to allow vapor (or condensed vapor, if any) to flow in to the condenser.

The Condenser:

The condenser specifications used here are entirely different from the one used by Lodl and Scheller. The specifications of the different tubes constituting the condenser are indicated in Figure 2 . This is essentially a Shell and Tube type with vapor condensing outside two concentric tubes through which cold water is circulated. Circulation of cold water is effected by means of a portable Helium cooler. Care is taken to see that all the vapors

that come from the contactor are condensed over atleast seventy five percent of the total length of the total condenser and hence do not stand any chance of getting into the manometer. As can be seen in Figure 4 , towards the bottom of the condenser a tube much smaller than the major diameter of the condenser is attached, which thus helps in allowing condensed vapor to come and mix with the liquid in the vaporizer and helps in connecting the condenser with the three way stop-cock. The condenser is connected to the pressure system by 8 mm.dia. glass tubes.

The Manometer:

A U-tube manometer made out of glass tube (5 mm i.d. and 9 mm o.d.) with tripple distilled mercury as the manometric liquid is used to measure the pressure in the system roughly. The manometer is about 90 Cms. long and can safely read from 0 to 760 mm mercury pressure to 0.05 mm . The manometer is connected to the condenser and the ebulliometer by glass tubing through a two-way glass stop-cock (shown in Figure 3).

The Ebulliometer:

A single-stage Swietoslawski ebulliometer (Swietoslawski W, Ebulliometric Measurements (1945)) is used to measure the accurately pressure. The various working components of this kind of ebulliometer is shown in Figure 3 in detail.

Essentially the ebulliometer consists of a boiling chamber B, a thermowell mounted in the chamber, A, connecting

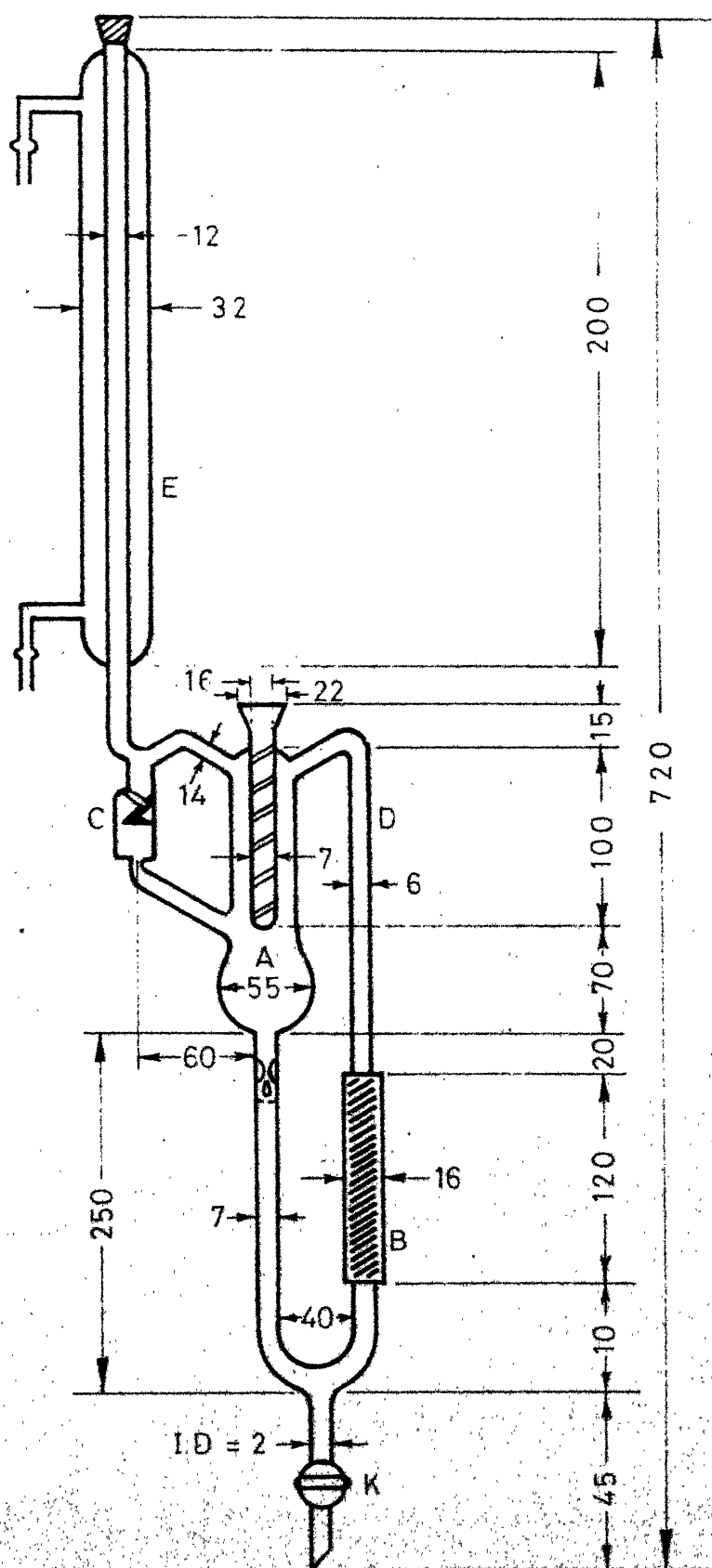


FIG. 3. SINGLE STAGE EBULLIOMETER

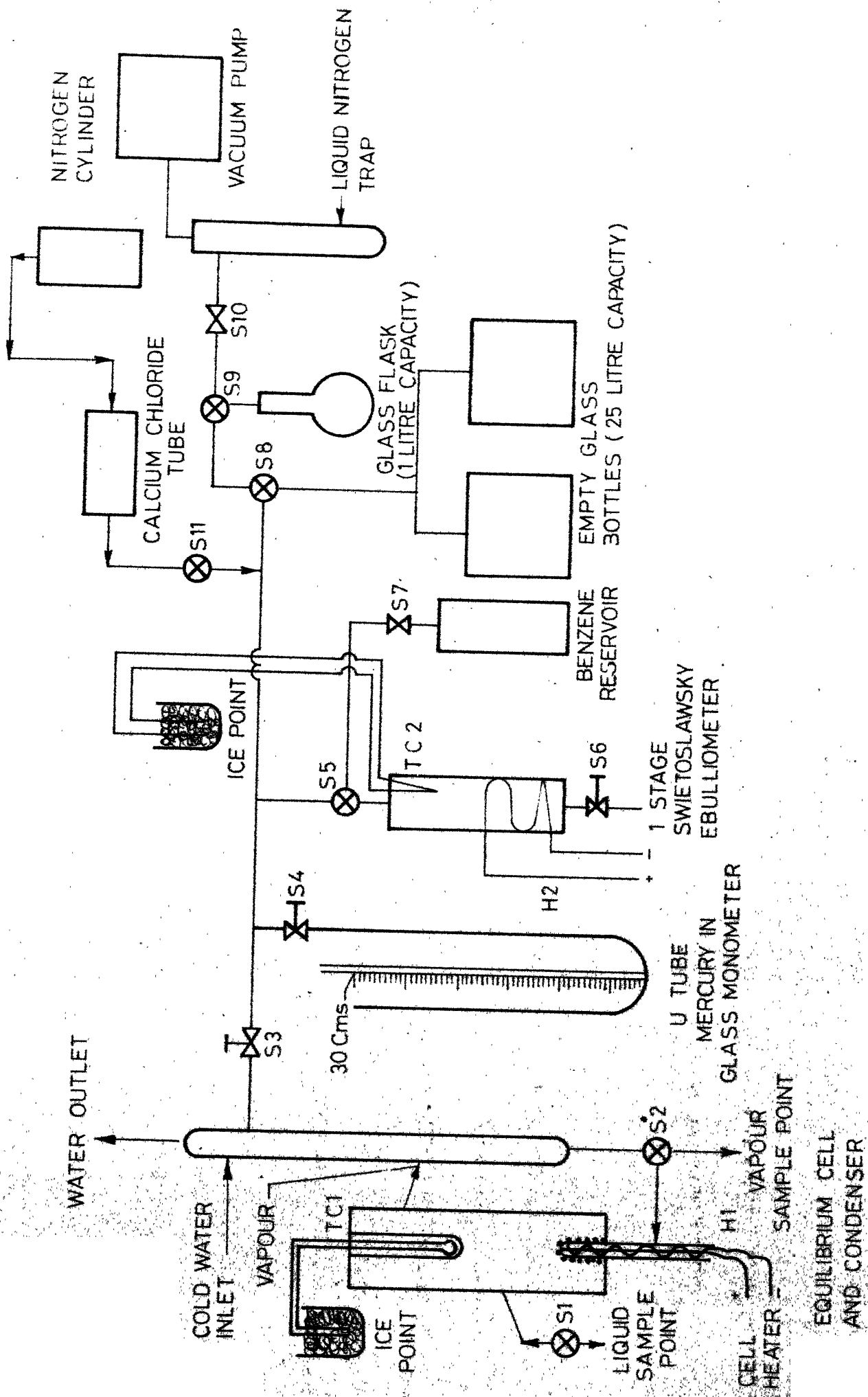


FIG.4 SCHEMATIC LINE DIAGRAM FOR THE EXPERIMENTAL SET-UP.

boiler by means of glass tube and opening to the condenser. The instrument function is as follows. The standard liquid (which is available easily in a very pure form and whose normal boiling point is accurately known) is filled into the boiler. The liquid is heated by means of an electric heater designed suitably to cause necessary boiling rate corresponding to the desired pressure. The bubbles of vapor carry with them slugs of liquid which spurt from the tube D to the thimble T as shown in Figure 3. Equilibrium between the liquid and the vapor phases is first established on this thimble; a small part of the falling superheated liquid vaporises at the expense of its sensible heat. As a result the temperature falls to the equilibrium value. Mercury is added to the thermowell to improve heat transfer with the thermocouple. The vapors of the liquid are condensed in the condenser E. The condensate flows into the drop counter C back into the boiling flask. It is easy to check the amount of liquid condensing in the condenser and thus the intensity of heating by means of the drop counter. The drop counter is nothing but a straight tube with a broad orifice bent at right angles. A short rod ending in a hemisphere of diameter about 4 mm is fused to its lower end. The drops form on the surface of this hemisphere. This kind of a drop counter is advantageous since a liquid seal is not formed and any pressure differences which may occur are rapidly evened out. A suitable intensity of heating is achieved by counting the

of droplets per minute in the counter. Boiling point is constant over wide range of intensity of heating. The rate of formation of drops should be 8 to 20 drops/minute. If the heat supply is in excess, the superheating of the boiling liquid is so great that the liquid on the well T is not able to reach equilibrium with its vapor. Hence a regulated heat supply is essential which is affected by regulating the voltage supply through a variac.

The boiling chamber, thermo well chamber and the intermediate connecting tubes are insulated by asbestos powder and asbestos rope to avoid heat loss by radiation.

For charging the liquid into the ebulliometer in order to avoid contact of air, a reservoir is mounted by the side of it connected to it by means of a 2-way stop cock. The liquid in the reservoir is heated by a heating coil (120 volts supply) and the vapor thus produced is condensed to the boiling chamber from the condenser. The ebulliometer is connected to the system by means of a 3-way stop-cock.

The Ballast:

The ballast consists of two 25 litre flasks perfectly sealed at the opening and kept closed inside a wooden frame and connected to the system by a 3-way glass stop cock. The function is to dampen the pressure fluctuation in the system.

The system is evacuated by a vacuum pump (Cenco Hyvac-7, made in U.S.A.) which is connected to the system by rubber

(Hyvac.) and glass tubes through a liquid nitrogen trap and a 500 cc (evacuated) flask.

Requisite pressure in the system is maintained by bleeding nitrogen gas into the system. Nitrogen from the cylinder passes through a calcium chloride tube and the controlled rate of supply of nitrogen to the system is affected by a needle valve. (Hoke, made in U.S.A.)

#####

CHAPTER 5

EXPERIMENTAL PROCEDURE

The entire experimental procedure adopted in this investigation can be enumerated in detail under the following headings:

1. Sample purity
2. Feeding of samples into the equilibrium still
3. Maintenance and measurement of pressure.
4. Measurement of (equilibrium) temperature
5. Operation of the still
6. Withdrawal of equilibrium sample.
7. Analysis of equilibrium samples

5.1 Sample Purity:

Methanol and Methylene chloride used in the present investigation were of AnalR grade. Methanol of 99.7 mole percent purity or better (water content 0.1 percent) was obtained from the British Drug Houses, Ltd., where as methylenechloride (water content 0.05 percent) was obtained from E. Merck Company, Germany.

The purity of the samples were checked by gas-liquid chromatography (GLC) with Varian Aerograph (Model 90-P) and they were found to comply to the company specifications and the samples were used without further purification. As is mentioned above this investigation for $\text{CH}_3\text{OH}-\text{CH}_2\text{Cl}_2$ system was attempted to make the data most useful to the

TABLE 1 - PHYSICAL PROPERTIES OF THE PURE SUBSTANCES

Refractive Index, n_D^{25}	<u>Methanol</u>	<u>Methylenechloride</u>
Experimental	1.3260	1.4212
Literature ()	1.32625	1.4219
Boiling point ($^{\circ}\text{C}$ at 550 mm. Hg. pressure)		
Experimental	55.95	30.98
Literature	55.98	31.01
Refractive Index n_D^{30}	<u>Toluene</u>	<u>Benzaldehyde</u>
Experimental	1.49126	1.54078
Literature	1.49125	
Boiling Point ($^{\circ}\text{C}$ at 760 mm. Hg. pressure)		
Experimental	110.62	179.01
Literature	110.625	179.00
Refractive Index, n_D^{25}	<u>Benzene</u>	
Experimental	1.49260	
Literature	1.49262	
Boiling Point ($^{\circ}\text{C}$ at 760 mm. Hg. pressure)		
Experimental	79.01	
Literature	79.00	

Hindustan Photo Films as they were interested in the recovery of the mixture ($\text{CH}_3\text{OH}-\text{CH}_2\text{Cl}_2$) in the presence of 1 percent water. Hence, no further attempt was made to purify the samples any further.

For the system Benzaldehyde-Toluene, the samples obtained were AnalR grade obtained from "Reanal" Finomvegyszergyar Budapest, Hungary and International Chemical Industries, India, respectively. Both samples, Benzaldehyde and toluene were of approximately 99.95 mole percent stated purity and was checked by GLC analysis. Benzaldehyde and toluene were found to be quite pure since it was observed that the physical properties like the normal boiling point and refractive index at 30°C were consistent with the literature data (37, 41) and hence no further attempts were made to purify the samples. The normal boiling point and the refractive index for the substances used in this investigation are reported in Table I.

5.2 Feeding the Samples in the Equilibrium Still:

Samples were fed into the vaporize and the contactor by means of a channel pump (DIAL A PUMP, DURRUM INST CORPN. made in U.S.A.) having 12 channels. Extreme care was taken to avoid contact of air with the samples while feeding. However, it was found difficult to avoid contact with air, and hence this system of feeding was changed. Sample was taken in a graduated cylinder and was fed into the still

at both the sections by bleeding in Nitrogen through the cylinder and maintaining a little vacuum in the system. This method of feeding was found to be extremely satisfactory. The samples were fed upto the marks as shown in Figure.

5.3 Maintenance and Measurement of Pressure;

To start with, valves S-1 and S-2 (Figure 4) were closed to outside and all other valves excluding S-5 to the ebulliometer and S-7 to the Benzene reservoir, were opened. The vacuum pump was run for about 2 hours to completely evacuate the system. Then the samples were fed into the still as described in 5.2. The required pressures 550 and 760 mm mercury pressure) were maintained in the system by bleeding in Nitrogen through the valve S-11 and closing the valve S-9 to the flask. The pressure was then roughly read on the manometer and the exact pressure was calculated at the equilibrium temperature in the ebulliometer. (Thermocouple TC-2). The heaters were turned on and throughout the experiment the ballast was kept open to the system. Thus any amount of fluctuation in pressure was dampened by the ballast. Initially due to nitrogen in the system being heated up, there was a rise in mercury level in the manometer. This was avoided by slowly opening the valve S-9 to the flask and hence adjusting the pressure. This kind of fluctuation was entirely absent at or around the equilibrium state. The accuracy of pressure measurement was estimated to be 0.01 mm mercury pressure.

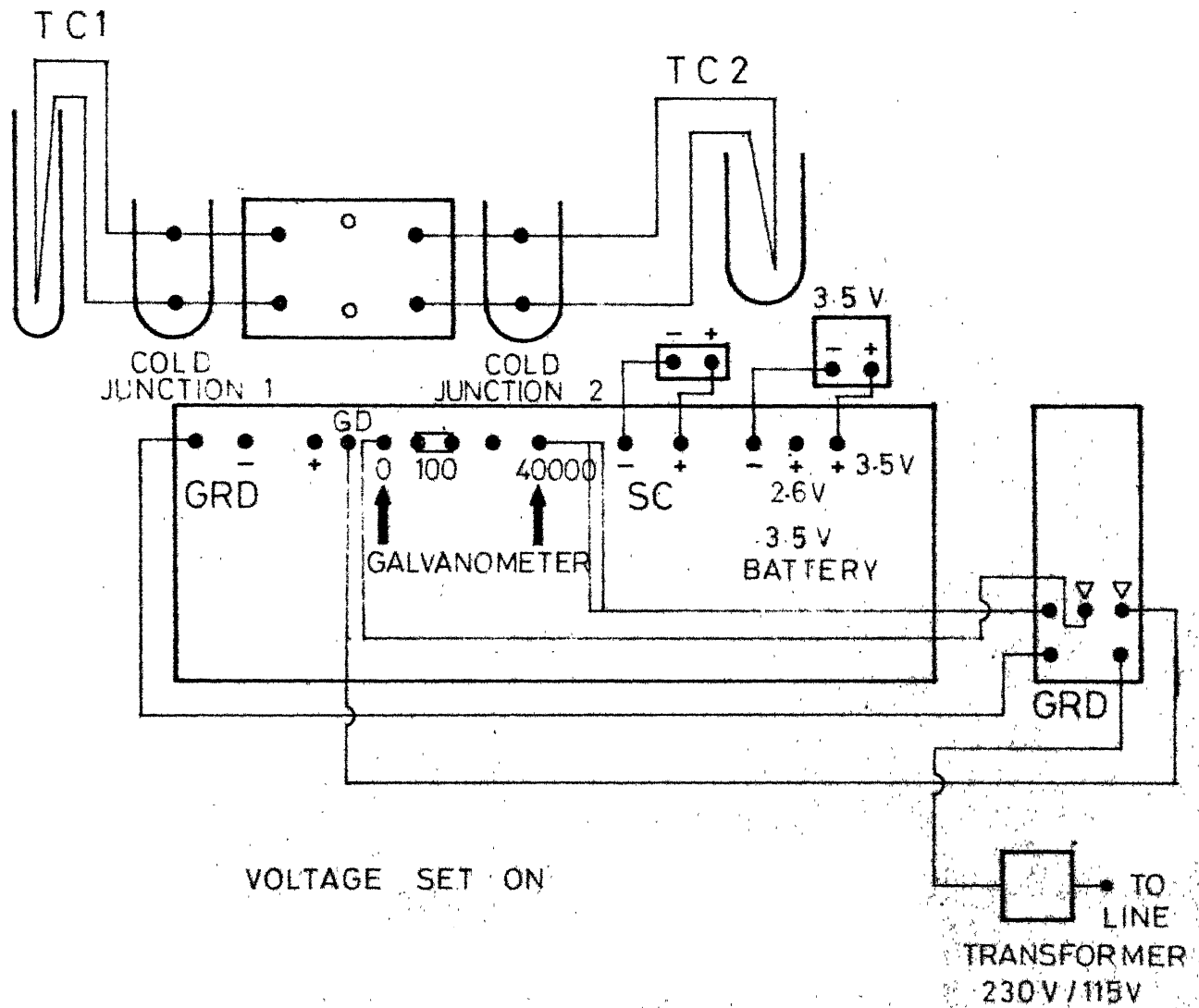


FIG.5 TEMPERATURE MEASUREMENT CIRCUIT.

5.4 Measurement of (Equilibrium) Temperature:

Accurate measurement of temperature was carried out by means of copper-constantan (Cu=60 percent, Ni=40%) thermocouples calibrated against a Leeds and Northrup platinum resistance thermometer (25 ohm). The voltage readings were taken by means of a K-3 universal potentiometer. (Leeds and Northrup, 7553 - 5 Type, made in U.S.A.). The copper constantan thermocouples were chosen because of the high thermal conductivity and low oxygen content of copper and the high operating range of 0 to 350°C. The connections were made as per the manual and the Standard Cell Voltage was set at 1.0185 adjusting against the yearly voltage drop. (original value being 1.01864 volts). Copper leads were used as the connecting wire. Calibration of thermocouples

Calibration of Thermocouples:

The thermocouples TC1 and TC2 were calibrated against a platinum resistance thermo unit by using a Sargent Thermonitor controlled constant temperature bath ($\pm 0.01^\circ\text{C}$). Ethylene glycol (upto 130°C) and "Mauua Oil" (upto 300°C) were used as bath fluids. The necessary circuit used for the calibration is shown in Figure .

The hot junctions of the thermocouples TC1 and TC2 were placed in constant temperature bath deeping about 6 inches inside the bath fluid and tied close to the platinum resistance thermometer. The cold junctions were maintained by a slurry of crushed ice and distilled water in deware flasks. Care was taken to avoid air pockets

in the slurry with a rod and time to time water was siphoned out by a polythene tube.

After the thermocouples were calibrated, the hot junctions were placed in the thermowells of the still and the ebulliometer and the cold junctions were maintained in the similar fashion. The potentiometer was capable of reading with a precision of 0.0001 percent or better (voltage reading) and the accuracy of the temperature measurement was found to be reproducible to atleast 0.01°C .

5.5 Operation of the Still:

After the samples were fed upto the marks in the still and requisite pressure was roughly read from the manometer, the heaters were put on and exact voltage was supplied for smooth operation. The voltage to the cell heater was however varied with feed composition while that to the ebulliometer at 550 mm mercury pressure and 760 mercury pressure was roughly 26 and 30 volts respectively. A controlled and exact voltage supply to the heaters (cell heater was made up of 2 meter length 24 gauge nichrome wire with a resistance of 7.8 ohms/meter while that of the ebulliometer cell was of 1 meter length with similar specifications). Could avoid bumping and result in required rate of condensation of vapor. Under ordinary working conditions, the liquid level in the vapor condensate return line was higher than the level in the vaporizer, so that the condensate is not contaminated by liquid from the vaporizer. The liquid in the vaporizer was

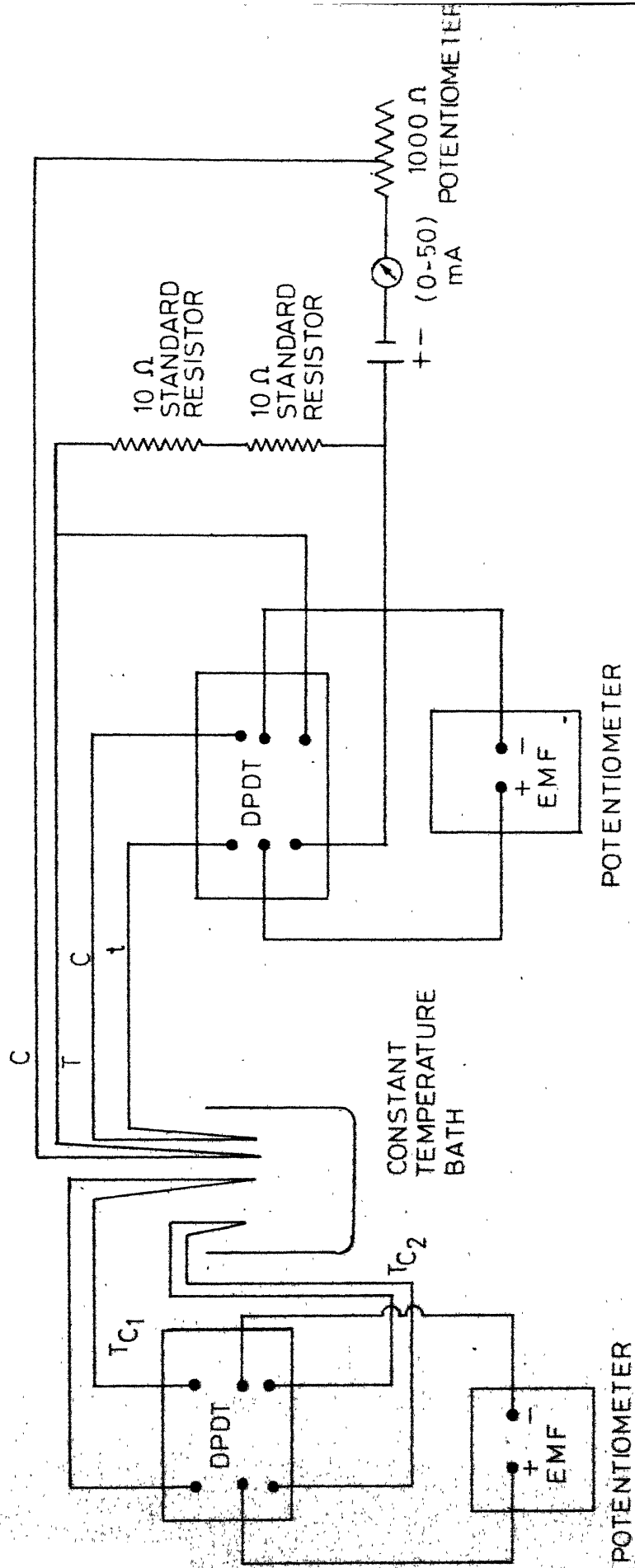


FIG. 6 THERMOCOUPLE CALIBRATION CIRCUIT

heated up by the heater and vapors thus produced bubbled through the contactor liquid passing through the slots made in the outer (8 in number) and inner (4 in number) walls of the contactor. Thus the more volatile component vaporized from the contactor and passed through the opening to the condenser and condensed back to the vaporiser. This closed cycle of operation was allowed to go on until equilibrium was reached which was ensured by a constant temperature readings by the thermocouples TC1 and TC2 over a period of half an hour. The rate of condensation of vapor from the cell was found to be 1 drop per 20 seconds (roughly). The time for equilibrium was 3 to 4 hours for $\text{CH}_3\text{OH}-\text{CH}_2\text{Cl}_2$ system and 2 hours for benzaldehyde-toluene system. For the latter system the rate of condensation was 1 drop/sec. The rate of condensation of benzene vapors in the ebullio-meter was found to be 20 drops/min.

Withdrawal of Equilibrium Samples

When equilibrium was ensured in the still by the constant voltage reading of the potentiometer, samples were ready to be withdrawn from the stop cocks S-1 and S-2. Before withdrawing the samples, valve S-1 was flushed with about 2 to 5 ml. of liquid and valve S-2 with about 3 ml. of liquid. This ensured that the samples withdrawn were actually the equilibrium samples. Care was taken in operating the 3-way stopcock S-2 in such a way that the sample was drawn from the condenser, instead of from the vaporizer.

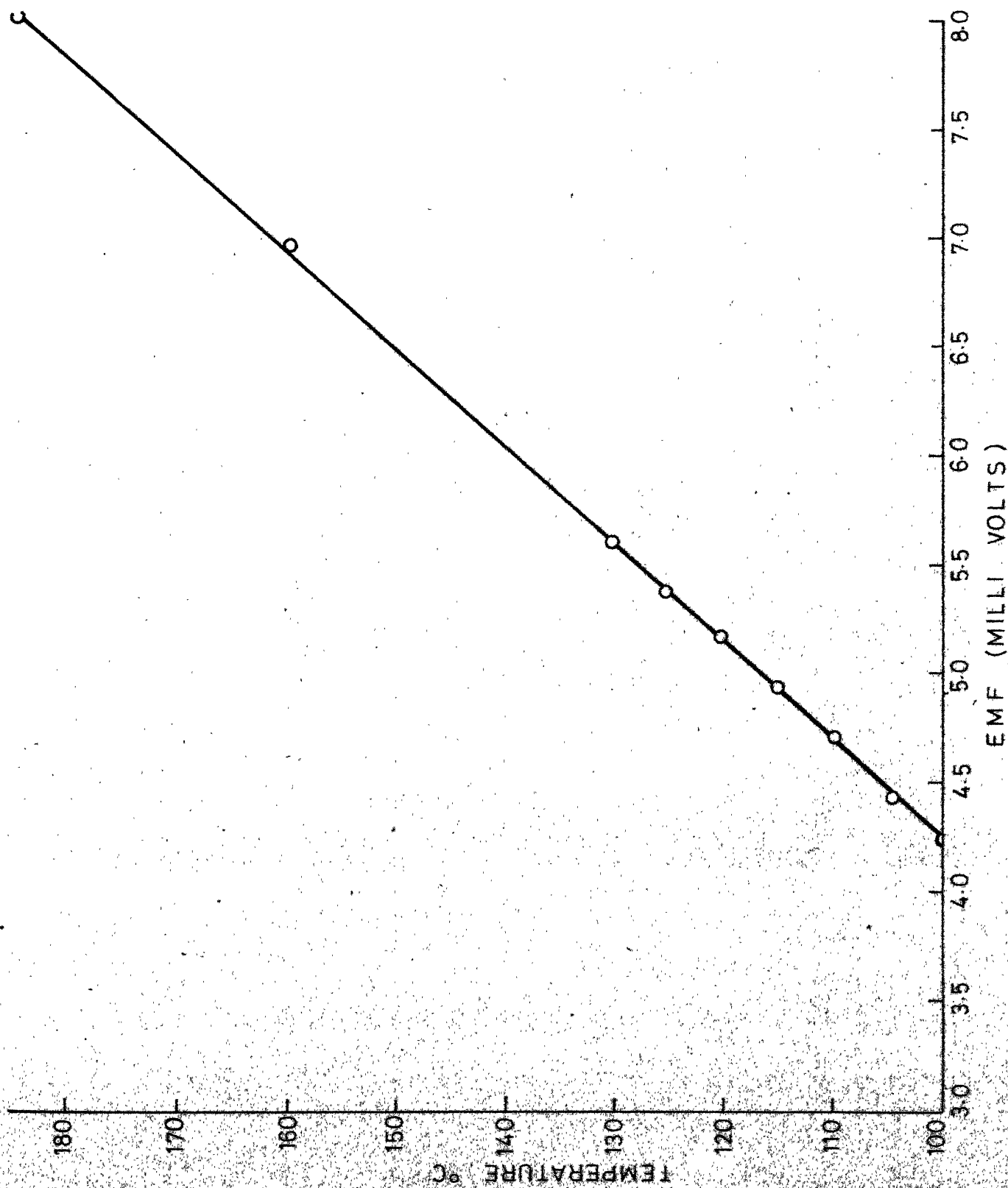


FIG. 7 a. EMF TEMPERATURE DIAGRAM USED FOR TOLUENE BENZALDEHYDE SYSTEM

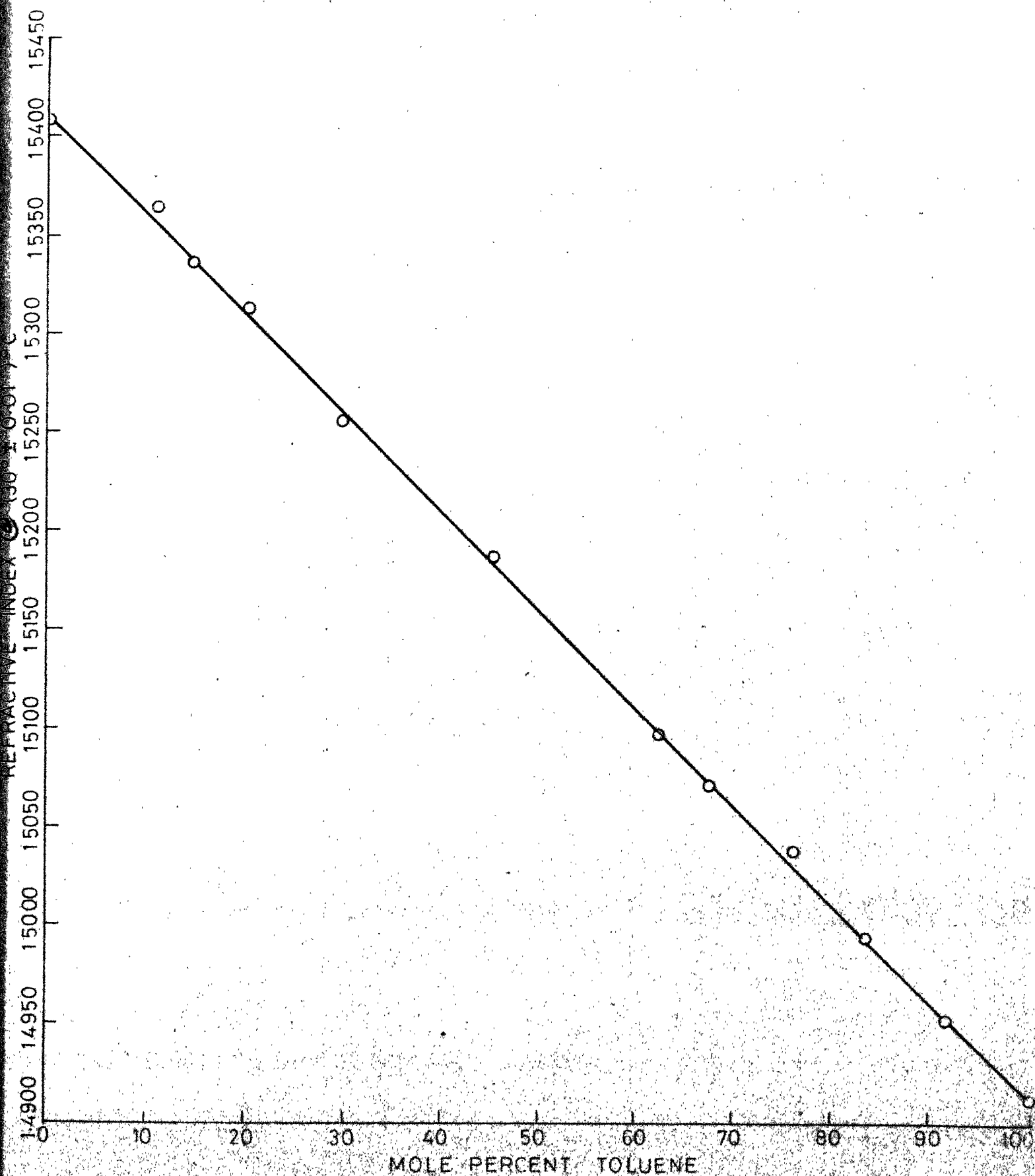


FIG 8.5 REFRACTOMETER CALIBRATION CURVE FOR TOLUENE - BENZALDEHYDE SYSTEM AT (30 ± 0.01) °C

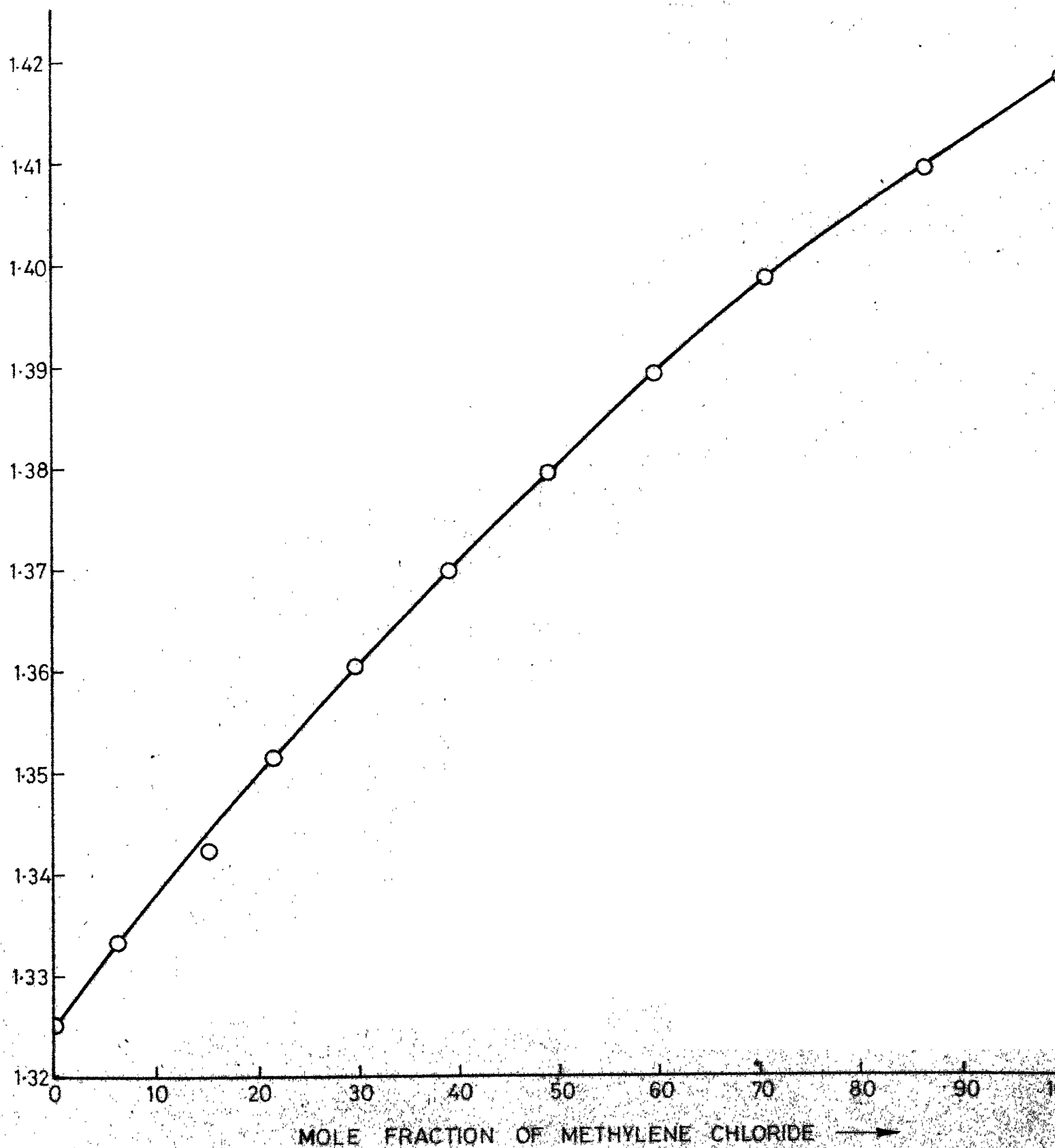


FIG. 8a. REFRACTIVE INDEX-COMPOSITION CALIBRATION CURVE FOR METHANOL-METHYLENE CHLORIDE SYSTEM AT $(25 \pm 0.01)^\circ\text{C}$

Since the vapor liquid equilibrium data for the methanol methylene chloride system was investigated at 550 mm mercury pressure, it was more desirable to increase the system pressure to slightly above atmospheric just before taking the samples. This rapid increase in pressure made possible by the 3-way valve in the vacuum line, immediately stopped the boiling in the cell, thus preventing any further change in compositions. In addition, it reduced the danger of flashing of methylene chloride when sampling at low pressure. However, this process of withdrawing the sample for the Benzaldehyde-Toluene system was not necessary, since the system was operated at 760 mm. mercury pressure and this pressure was normally more than the atmospheric pressure of 755 mm mercury pressure.

Since methanol and methylene chloride were fairly low boiling compounds at atmospheric as well as 550 mm. mercury pressure, to prevent the loss of compounds during sampling process by evaporation, they were collected in crushed ice bath.

Analysis of Equilibrium Samples:

Immediately after the samples were withdrawn, they were analysed for composition by a "Bausch and Lomb" 3L-... refractrometer which was calibrated previously as shown in the Appendix 3(a)&3(b). The refractrometer could read upto 4 significant figures with an estimated fifth place and hence the mole fraction was reproducible to atleast 0.001. The refractive index composition data for methanol-methylene

chloride system was reported at $25 \pm 0.01^{\circ}\text{C}$ and that for the Benzaldehyde-Toluene system was reported at $30 \pm 0.01^{\circ}\text{C}$. The temperatures were maintained in the prism by circulating distilled water from a sargent constant temperature bath. There was absolutely no problem in maintaining 25°C in the prism since the then room temperature was about 20 to 22°C (December) while it posed a little problem in maintaining a temperature of 30°C since the then room temperature was about 36°C (April). However this problem was eliminated by bringing down the temperature by a freezing mixture in the bath.

CHAPTER 6

EXPERIMENTAL RESULTS

The calculation procedure was followed using Prausnitz method as to calculate the activity coefficients taking the vapor phase non-ideality into consideration (Chapter 3). This is one of the striking features of this work since in almost all the previous works of this nature vapor phase is assumed to be ideal at normal operating pressures. The liquid molal volumes for methanol was obtained from reference (MCA). Over a range of 0 to 100 which was well above the range of temperature dealt with in the calculations and the intermediate values were interpolated by plotting a graph of density versus temperature. The density data for the methylene chloride was not available in the literature over the entire working temperature range and hence they were predicted by the Yen and Woods procedure(47). The same procedure was adopted for predicting the density for Benzaldehyde and for Toluene.

The virial coefficients for methylene chloride and methanol were obtained from Masia et.al. (23) and Kudchadker et. al. (21) respectively. The values of intermediate temperatures were obtained by interpolation. For Benzaldehyde and for toluene, the virial coefficients were obtained by Pitzer's correlation (30). The critical constants T_c , P_c , V_c for toluene and T_c , P_c for benzaldehyde were taken from Kudchadker et.al (20) review paper.

TABLE 2. - EXPERIMENTAL DATA FOR METHANOL - METHYLENE
CHLORIDE SYSTEM AT 550 mm.Hg Pressure

Run No.	Time taken (Hrs.)	Thermocouple readings		Refractive Index at $(25 \pm 0.01)^\circ\text{C}$	
		TC ₁ (Volts)	TC ₂ (Volts)	Liquid sample (X ₁)	Vapor Sample (Y ₁)
1	3½	0.0022985	0.0028382	1.3260	1.3260
22	4	0.002284	0.002840	1.32725	1.32875
23	3	0.002282	0.002834	1.3275	1.32902
24	3½	0.0021845	0.002836	1.3296	1.3376
3	3½	0.0021142	0.002838	1.3415	1.3465
6	3	0.0019673	0.002838	1.34159	1.3568
8	3	0.00185825	0.002838	1.3425	1.35851
26	3	0.001791	0.002836	1.3487	1.3676
11	3½	0.001705	0.002835	1.35825	1.37548
2	3½	0.001594	0.002837	1.3640	1.3835
5	3½	0.001505	0.002834	1.3720	1.3891
7	3	0.0014125	0.002838	1.3810	1.3958
10	3½	0.0013125	0.002836	1.3920	1.4010
4	3	0.001280	0.002835	1.3960	1.4028
18	3	0.0011572	0.002838	1.4114	1.4120
19	3	0.0011582	0.002837	1.4134	1.4125
20	3½	0.0011602	0.002835	1.41475	1.4130
21	3½	0.0011665	0.002838	1.41495	1.41320
30	3	0.001208	0.002838	1.4205	1.4165
31	3½	0.001201	0.002838	1.4212	1.4212

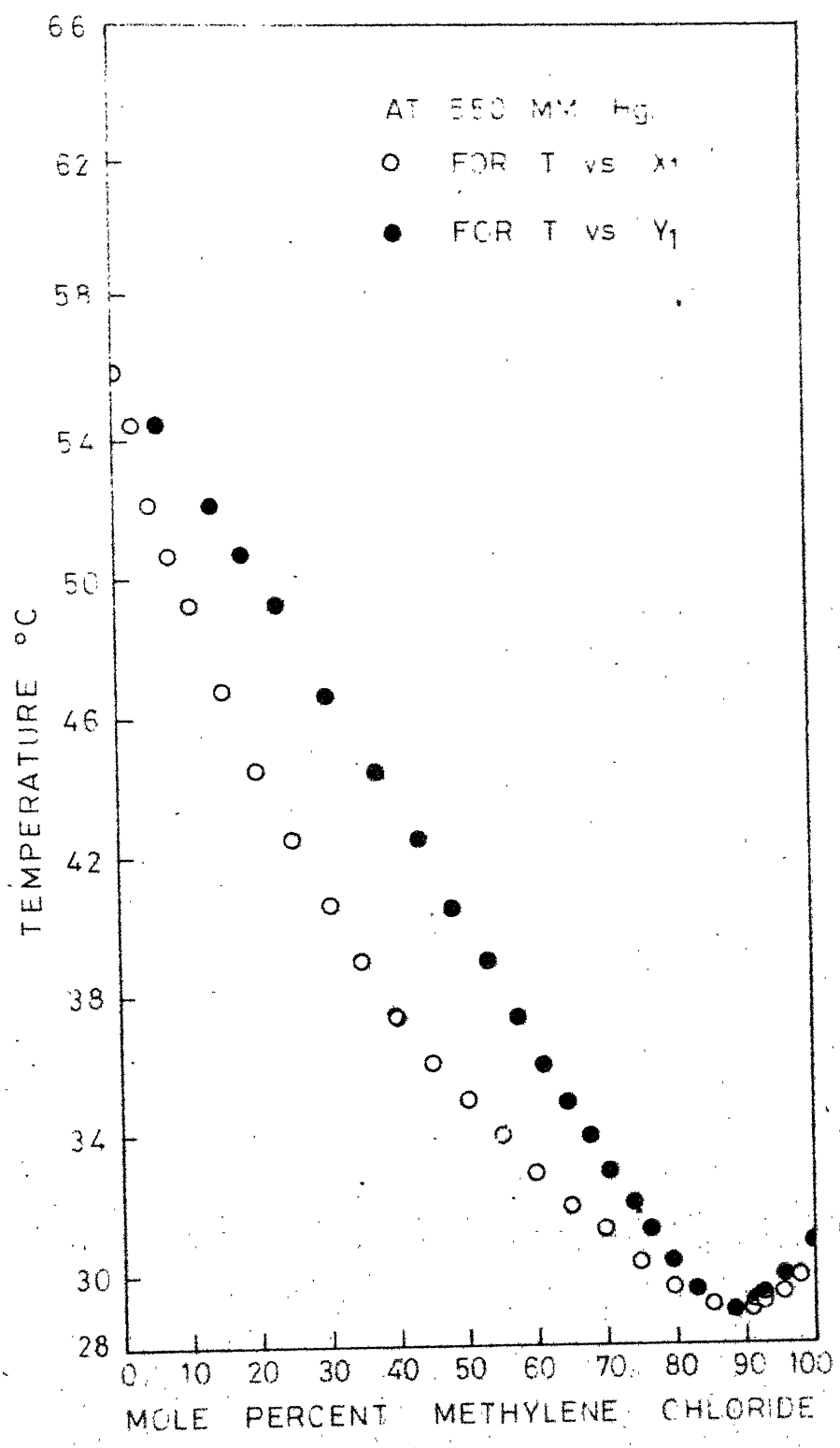


FIG 9 BOILING POINT COMPOSITION DIAGRAM FOR METHANOL-METHYLENE CHLORIDE SYSTEM

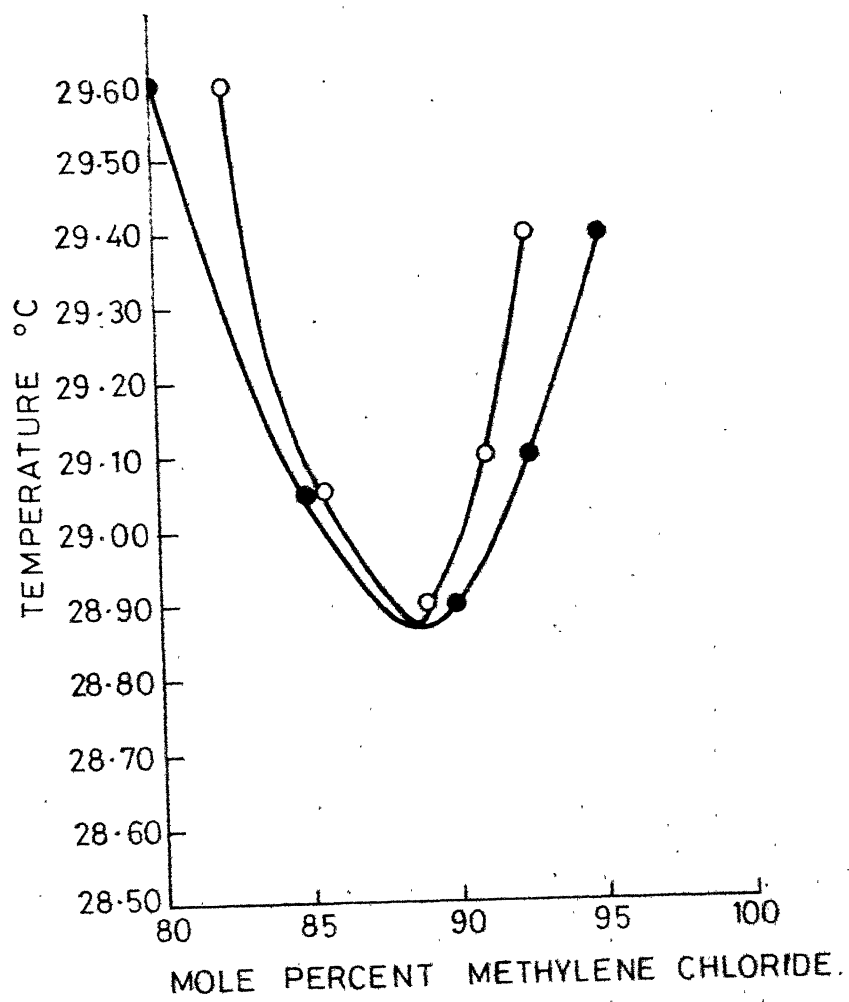


FIG. 9 a. ENLARGED DIAGRAM OF AZEOTROPIC POINT AT 550 mm. MERCURY PRESSURE.

TABLE 3 - EXPERIMENTAL DATA FOR TOLUENE-
BENZALDEHYDE SYSTEM AT 760 mm.Hg. PRESSURE

Run No.	Time in Hrs for Equilibrium	Thermocouple Reading		Refractive Index Reading(at $(30+0.04)^{\circ}\text{C}$)	
		TC ₁ Volts	TC ₂ Volts	Liquid Sample	Vapor Sample
1	$2\frac{1}{2}$	0.0047395	0.0033085	1.49125	1.49125
4	2	0.004902	0.0033090	1.4970	1.4927
5	$2\frac{1}{2}$	0.004995	0.003308	1.5022	1.4937
6	3	0.0051038	0.0033085	1.5089	1.4962
11	$2\frac{1}{2}$	0.0054325	0.0033085	1.5158	1.4997
5	2	0.0056075	0.003309	1.5206	1.5033
10	2	0.005909	0.003308	1.52403	1.5059
7	$2\frac{1}{2}$	0.006030	0.003079	1.5260	1.50748
3	3	0.0063025	0.0033075	1.5290	1.5110
18	3	0.0064910	0.003308	1.53125	1.5133
12	3	0.006710	0.0033102	1.53312	1.5165
17	$2\frac{1}{2}$	0.0069025	0.0033102	1.5347	1.51981
15	2	0.0071013	0.003310	1.5356	1.5223
2	2	0.0074025	0.0033078	1.5388	1.5290
14	$2\frac{1}{2}$	0.0076025	0.0033085	1.5401	1.53376
9	2	0.76075	0.003309	1.5413	1.53625
16	$2\frac{1}{2}$	0.0079802	0.003308	1.54079	1.54078

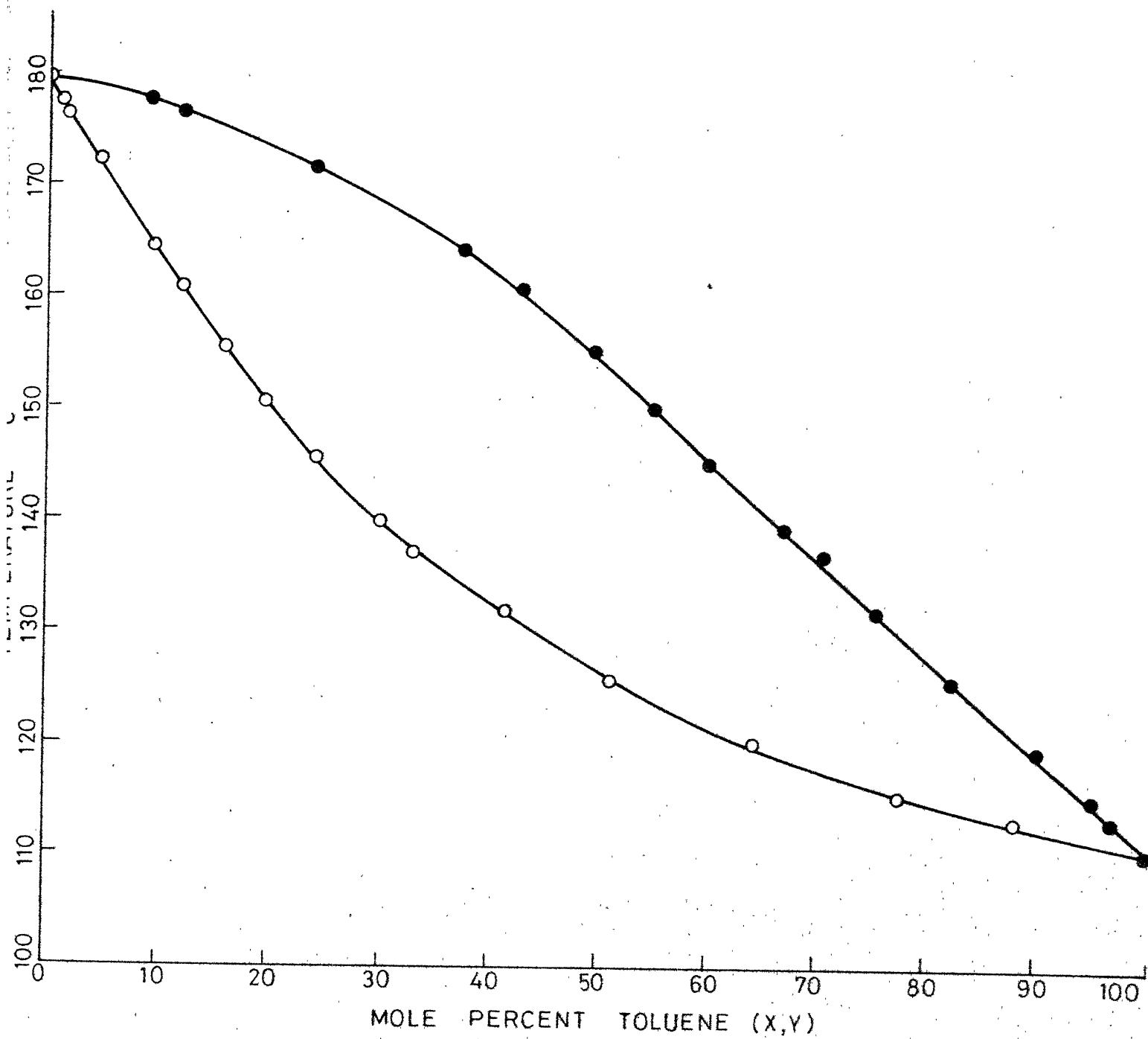
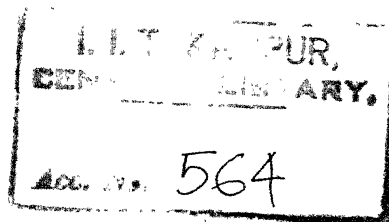


FIG. 10. TEMPERATURE COMPOSITION DIAGRAM FOR TOLUENE - BENZALDEHYDE SYSTEM AT 760 mm. Hg. PRESSURE.

TABLE 4 - EXPERIMENTAL T-X-Y D.T. FOR METHANOL -
METHYLENE CHLORIDE SYSTEM AT 550 mm.Hg. PRESSURE

Run No.	t. ₀ C	Mole fraction of CH ₂ Cl ₂ in liquid (X ₁)	Mole fraction of CH ₂ Cl ₂ in vapor (Y ₁)
1	55.93	0.000	0.000
22	55.65	0.014	0.025
23	55.55	0.0165	0.0270
24.	53.30	0.035	0.0975
3	51.65	0.06	0.1725
6	48.16	0.1325	0.2625
8	46.35	0.1598	0.3175
26	43.99	0.19	0.3655
11	41.95	0.275	0.4448
2	39.25	0.3425	0.5225
5	37.20	0.4100	0.5810
7	35.15	0.4950	0.6500
10	32.70	0.6125	0.7200
4	31.94	0.6600	0.7430
18	28.94	0.8800	0.8900
19	28.99	0.9100	0.9000
20	29.02	0.9300	0.9050
21	29.18	0.9350	0.9100
30	30.05	0.976	0.925
31	30.98	1.000	1.000



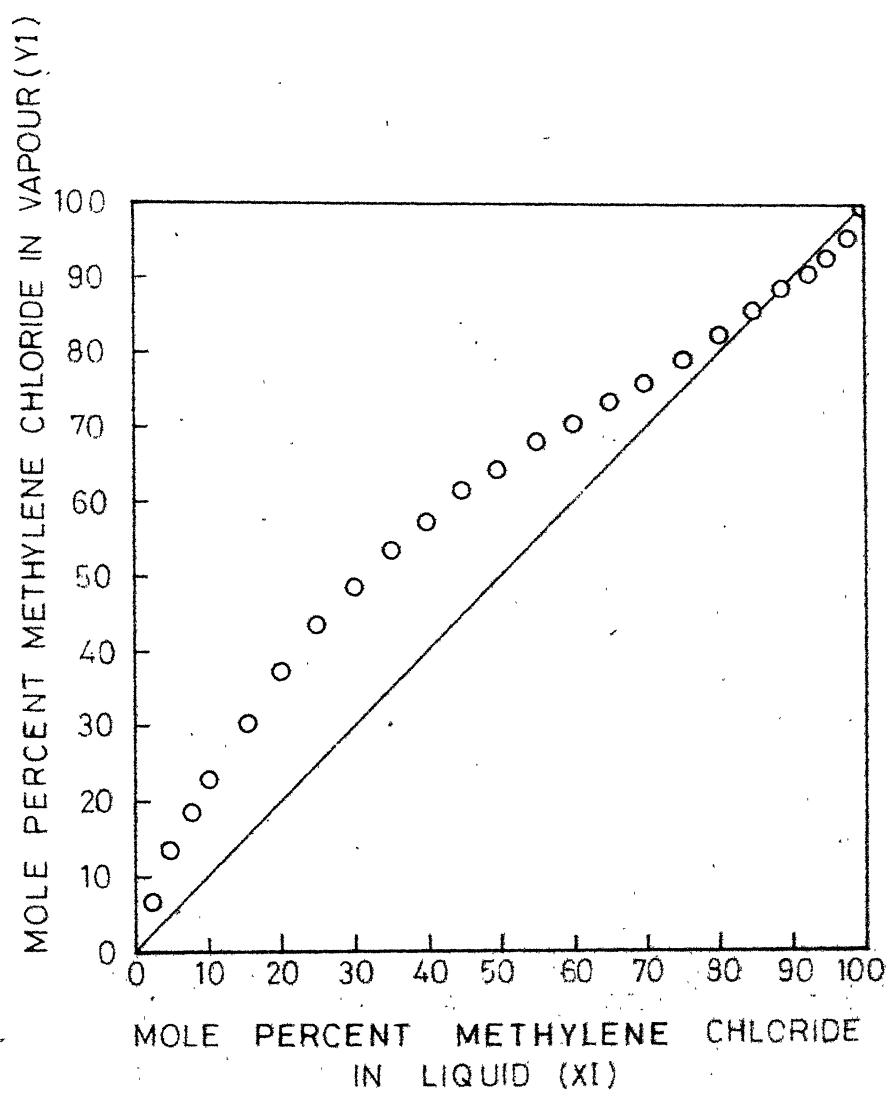


FIG.11. EQUILIBRIUM COMPOSITION DIAGRAM FOR
METHANOL-METHYLENE CHLORIDE SYSTEM
AT 550 MM. Hg.

TABLE 5 - EXPERIMENTAL ϕ - χ - ψ DATA FOR TOLUENE -
 BENZALDEHYDE SYSTEM AT 760 mm. Hg. PRESSURE

$t, ^\circ\text{C}$	χ	Mole fraction toluene in liquid	ψ	Mole fraction toluene in vapor
179.01		0.000		0.000
177.05		0.010		0.095
176.25		0.017		0.1425
171.75		0.049		0.240
164.65		0.097		0.328
160.65		0.122		0.427
155.40		0.158		0.492
150.30		0.195		0.549
145.60		0.241		0.602
139.75		0.301		0.672
137.05		0.331		0.705
132.01		0.410		0.755
126.00		0.511		0.825
119.80		0.646		0.898
115.50		0.776		0.951
113.60		0.8825		0.971
110.62		1.000		1.000

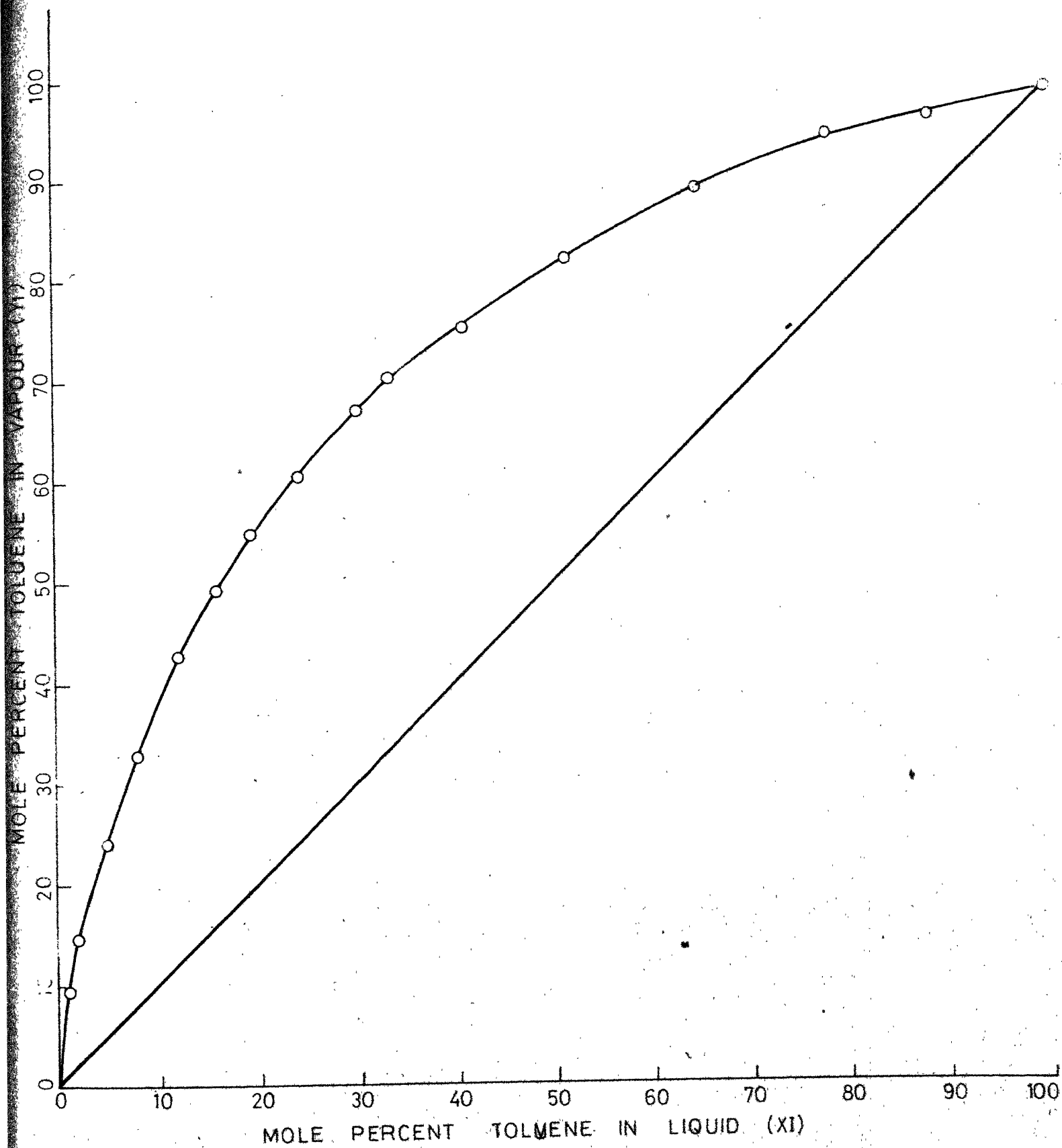


FIG. 12. Y-X DIAGRAM FOR TOLUENE-BENZALDEHYDE SYSTEM AT 760 mm. MERCURY PRESSURE.

TABLE 6. - SMOOTHED T - X - Y DATA FOR METHANOL- METHYLENECHLORIDE
AT 550 mm.Hg. PRESSURE

t °C	At (25 ± 0.01)°C	
	X	Y
55.95	0.000	0.0000
54.45	0.025	0.0650
52.25	0.050	0.1360
50.70	0.075	0.1850
49.21	0.100	0.2300
46.70	0.150	0.3050
44.58	0.200	0.3750
42.50	0.250	0.4325
40.62	0.300	0.4860
39.00	0.350	0.5325
37.48	0.400	0.5775
36.15	0.450	0.6145
34.95	0.500	0.6485
33.90	0.550	0.6800
32.95	0.600	0.7100
32.05	0.650	0.7385
31.28	0.700	0.7675
30.35	0.750	0.7945
29.60	0.800	0.8235
29.05	0.850	0.8555
28.88	0.885	0.8850
28.90	0.900	0.8875
29.10	0.925	0.9100
29.40	0.950	0.9270
29.95	0.975	0.9585
30.98	1.000	1.0000

TABLE 7 - SMOOTHED T-X-Y DATA FOR TOLUENE
BENZALDEHYDE SYSTEM AT 760 mm.Hg.PRESSURE

$t, ^\circ\text{C}$	x_1	y_1
178.0	0.006	0.06
177.0	0.013	0.10
176.0	0.019	0.134
175.0	0.026	0.166
174.0	0.032	0.194
172.0	0.045	0.236
170.0	0.058	0.281
165.0	0.091	0.364
160.0	0.124	0.44
155.0	0.158	0.503
150.0	0.196	0.557
145.0	0.242	0.6125
140.0	0.299	0.675
135.0	0.362	0.725
130.0	0.445	0.78
125.0	0.525	0.81
120.0	0.655	0.880
118.0	0.713	0.890
116.0	0.772	0.905
114.0	0.860	0.950
112.0	0.940	0.965

The V_c for benzaldehyde was predicted using T_c , P_c and the vander Waals constants a and b $(P + \frac{a}{v^2})(v-b) = RT$.

It was observed that the methanol-methylene chloride system exhibited a minimum boiling azeotrope at 28.88°C at a composition of 0.885 methylene chloride. This can be compared with the values obtained by Tenn and Missen (40) at 750 mm Hg. with azeotropic temperature of 37.2°C and composition of 0.846 methylene chloride and by Sarma (35) at 760 mm mercury pressure giving an azeotropic temperature of 38.80°C and composition of 0.805 methylene chloride.

are

The experimental results/given in Table 2 and 3 and are shown in Figures. 9 and 10.

#####

CHAPTER 7

CALCULATION OF DERIVED THERMODYNAMIC PROPERTIES

From the observed T-x-y values, the activity coefficients were calculated taking the vapor phase non-ideality into consideration for which the fugacity coefficients at each experimental point were calculated according to the Prausnitz method(31) from the smoothened data. The other important thermodynamic properties like relative volatility (and hence the K values) were also calculated and are tabulated in Table 16. The excess thermodynamic properties like excess Gibbs energy and excess enthalpy were calculated and are tabulated in Table 12 .

The third order γ -equation (10) was fitted to the experimental data of methanol-methylene chloride system and the fit was found to be satisfactory.

The γ -equation for a two component system is;

$$\gamma_{12} = \frac{1 + a_{12}x_2 + a_{122}x_2^2}{1 + a_{21}x_1 + a_{211}x_1^2} \quad (35)$$

where a_{12} , a_{21} , a_{122} and a_{211} are constants characteristics of the given binary system. Simplifying further

$$\gamma_{12} = 1 + a_{12}x_2 + a_{122}x_2^2 - a_{21}(x_1\alpha_{12}) - a_{211}(x_1^2\alpha_{12}) \quad (36)$$

Equation 36 can be represented in terms of activity coefficients as follows.

Activity coefficient of components 1 and 2 are given by

$$\gamma_1 = \frac{\Phi_1 P y_1}{x_1 f_1^{OL}} \quad (37)$$

and $\gamma_2 = \frac{\Phi_2 P y_2}{x_2 f_2^{OL}} \quad (38)$

Dividing equation (37) by (38);

$$\begin{aligned} \gamma_1/\gamma_2 &= \frac{\Phi_1 y_1 x_2 f_2^{OL}}{\Phi_2 y_2 x_1 f_1^{OL}} \\ &= \left[\frac{y_1/x_1}{y_2/x_2} \right] \left(\frac{\Phi_1}{\Phi_2} \right) \left(\frac{f_2^{OL}}{f_1^{OL}} \right) \\ \text{or } \gamma_1/\gamma_2 &= \gamma_{12} \left(\frac{y_1}{y_2} \right) \left(\frac{f_2^{OL}}{f_1^{OL}} \right) \end{aligned} \quad (39)$$

Combining Equations (35) and (39)

$$\gamma_1/\gamma_2 = \left(\frac{1 + c_{12} x_2 + c_{122} x_2^2}{1 + c_{21} x_1 + c_{211} x_1^2} \right) \left(\frac{\Phi_1}{\Phi_2} \right) \left(\frac{f_2^{OL}}{f_1^{OL}} \right) \quad (40)$$

$$\text{or } \left(\frac{y_1}{y_2} \right) \left(\frac{f_2^{OL}}{f_1^{OL}} \right) \left(\frac{\Phi_2}{\Phi_1} \right) = \left[\frac{1 + c_{12} x_2 + c_{122} x_2^2}{1 + c_{21} x_1 + c_{211} x_1^2} \right] \quad (41)$$

The constants a_{12} , a_{122} , a_{21} , a_{211} in Eqn.(41) were determined by the least squares regression analysis using the experimental vapor-liquid equilibrium data. The constants obtained are the following.

Methanol-methylene chloride system

$$a_{12} = 4.501$$

$$a_{122} = -2.555$$

$$a_{21} = -1.239$$

$$a_{211} = 0.762$$

Average deviation = ± 0.18

Maximum deviation = 17.91%

TABLE 8. - ACTIVITY COEFFICIENTS OF METHANOL
 IN METHYLENE CHLORIDE SYSTEM AT 550 mm. Hg. PRESSURE

x_1	γ_1	γ_2
0.000		1.0318
0.025	1.2532	1.0542
0.050	1.3927	1.0994
0.075	1.3208	1.1406
0.100	1.2860	1.1842
0.150	1.2247	1.2704
0.200	1.2036	1.3429
0.250	1.1858	1.4399
0.300	1.1793	1.5337
0.350	1.1677	1.6322
0.400	1.1653	1.7308
0.450	1.1527	1.8489
0.500	1.1408	1.9798
0.550	1.1276	2.1229
0.600	1.1156	2.2848
0.650	1.1056	2.4796
0.700	1.0963	2.6955
0.750	1.0955	3.0209
0.800	1.0938	3.4001
0.850	1.0905	3.8537
0.885	1.0893	4.0710
0.900	1.0733	4.5772
0.925	1.0617	4.8611
0.950	1.0406	5.8513
0.975	1.0259	6.5255
1.000	1.0031	

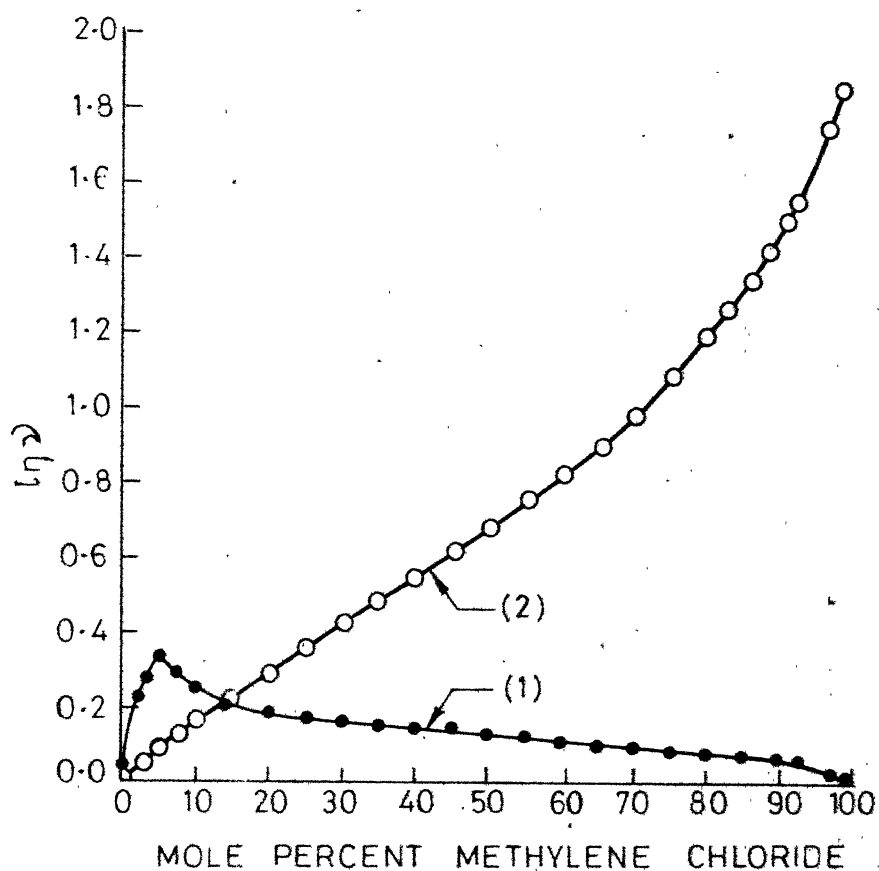


FIG. 13. ACTIVITY COEFFICIENT COMPOSITION
DIAGRAM FOR METHANOL (2)
METHYLENE CHLORIDE (1) SYSTEM AT
550 mm MERCURY PRESSURE.

TABLE 9 - ACTIVITY COEFFICIENT COMPOSITION DATA
OF TOLUENE-BENZALDEHYDE SYSTEM AT 760 mm.Hg.
PRESSURE

$t, ^\circ\text{K}$	γ	Gama 1	γ	Gama 2
451.15		2.6395		.9610
450.15		2.0441		.9509
449.15		1.8910		.9450
448.15		1.7290		.9414
447.15		1.6605		.9404
445.15		1.4758		.9536
443.15		1.4009		.9617
438.15		1.2507		1.0152
433.15		1.2068		1.0748
428.15		1.1856		1.1557
423.15		1.1655		1.3339
418.15		1.1466		1.3832
413.15		1.1349		1.4923
408.15		1.1235		1.6606
403.15		1.1015		1.8483
398.15		1.0942		2.5554
393.15		1.0763		2.4439
391.15		1.0531		2.9234
389.15		1.0419		3.4660
387.15		1.0337		3.3132
395.15		1.740		5.9341

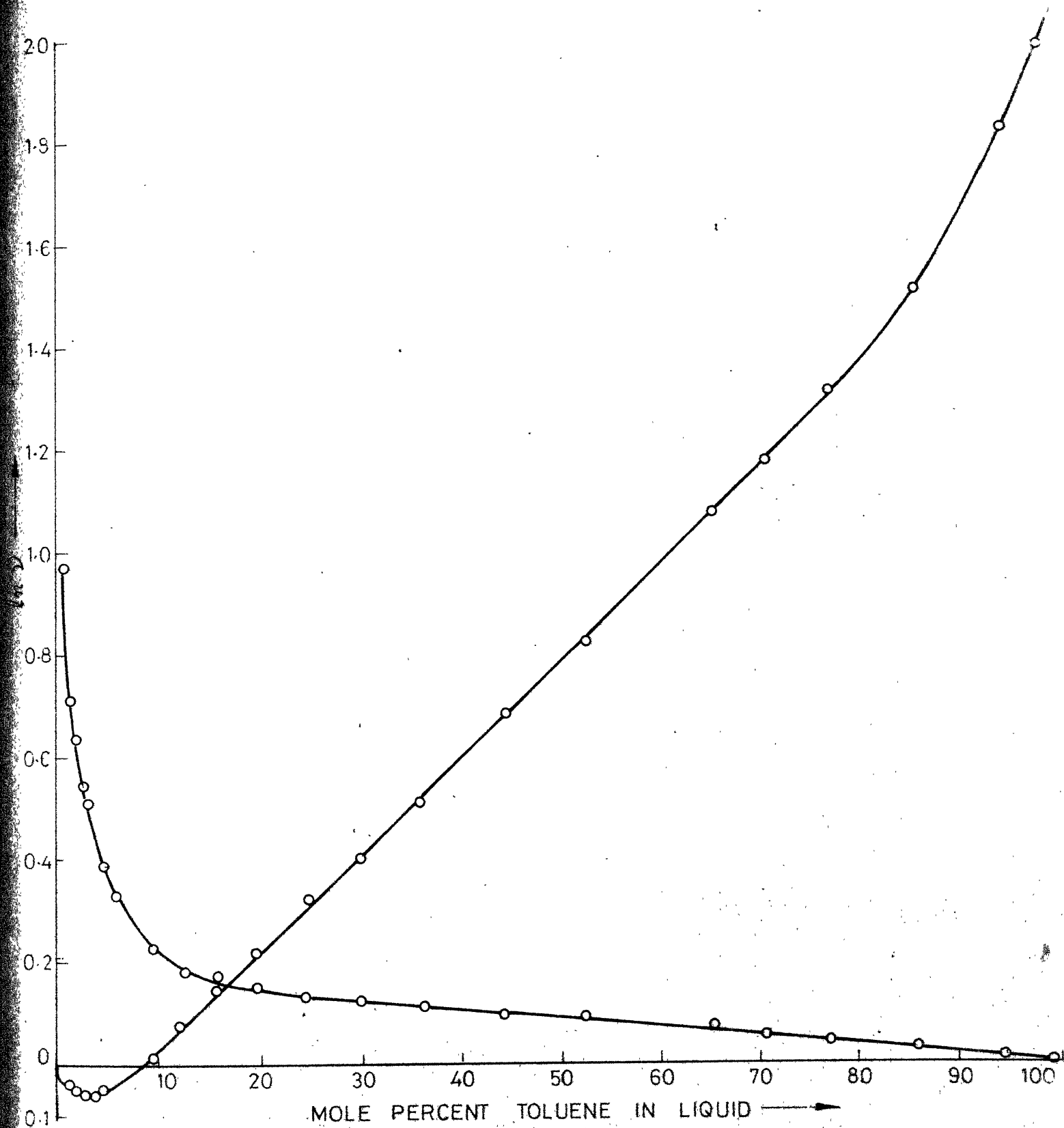


FIG. 14. ACTIVITY COEFFICIENT COMPOSITION DIAGRAM FOR TOLUENE-BENZALDEHYDE SYSTEM AT 760 MM MERCURY PRESSURE.

TABLE 10 - CALCULATION OF RELATIVE VOLATILITY FOR
Methanol-Methylenechloride at 550 mm.Hg. Pressure

X_1 CH ₂ Cl ₂ in Liquid	K_1 ($=Y_1/X_1$)	K_2 ($=Y_2/X_2$)	α ($=K_1/K_2$)
0.025	2.6000	0.959	2.7112
0.05	2.72	0.9095	2.9907
0.075	2.4667	0.8811	2.7996
0.10	2.3	0.8556	2.6883
0.15	2.0333	0.8176	2.4868
0.2	1.875	0.7813	2.4126
0.25	1.73	0.7567	2.2863
0.3	1.62	0.7343	2.2062
0.35	1.5214	0.7192	2.1154
0.40	1.4437	0.7042	2.0503
0.45	1.3656	0.7009	1.9483
0.50	1.297	0.7030	1.845
0.55	1.2364	0.7111	1.7386
0.60	1.1833	0.725	1.6322
0.65	1.1362	0.7471	1.5207
0.70	1.0964	0.775	1.4147
0.75	1.0593	0.822	1.2887
0.80	1.0294	0.8825	1.1664
0.85	1.0065	0.9633	1.0448
0.885	1.0000	1.0000	1.0000
0.925	0.9338	1.20	0.8198
0.975	0.9803	1.7680	0.5545

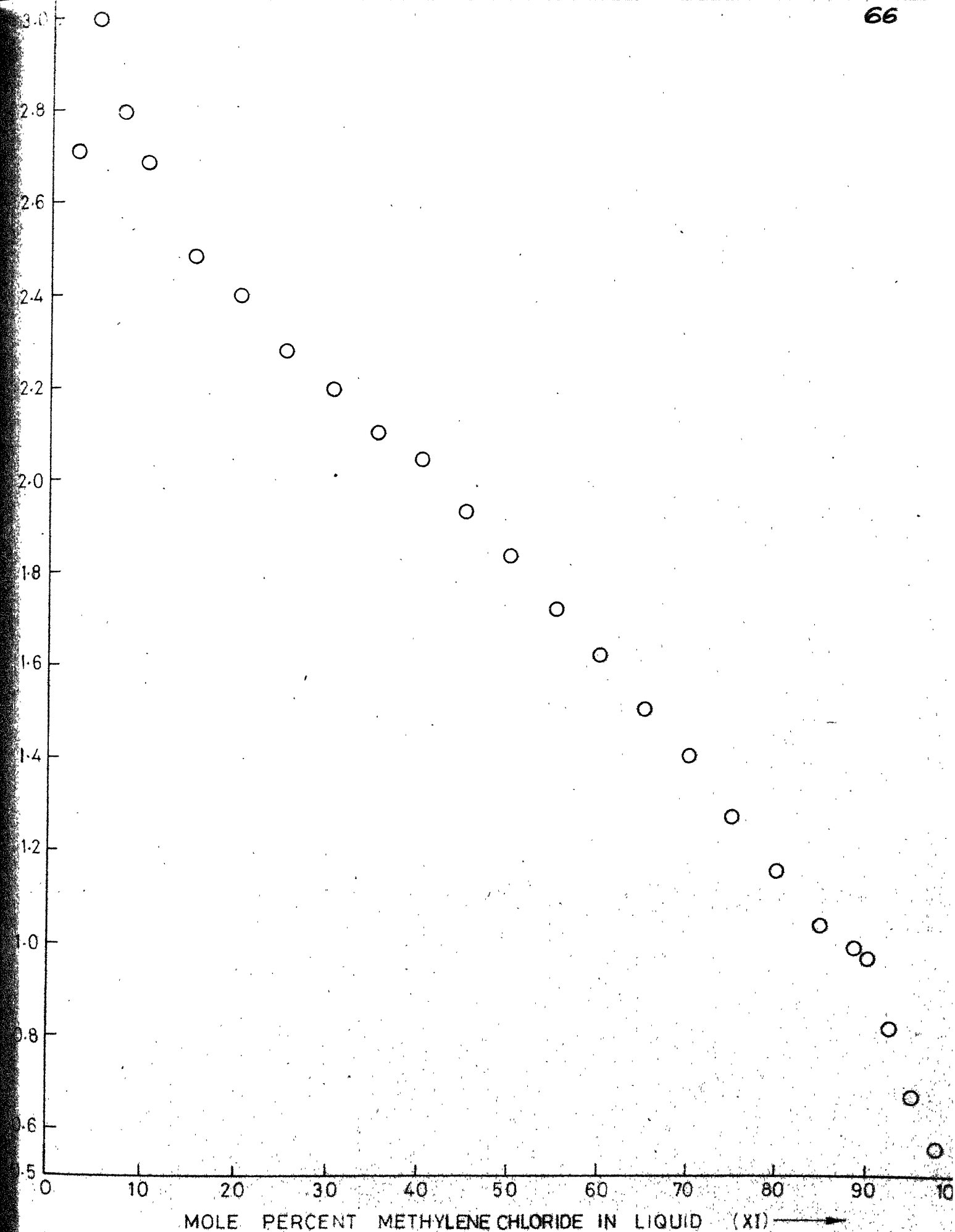


FIG. 15. COMPOSITION RELATIVE VOLATILITY DIAGRAM FOR METHANOL-METHYLENE CHLORIDE SYSTEM AT 550 MM Hg PRESSURE.

TABLE 11⁵ - RELATIVE VOLATILITY AND 'K' VALUES FOR
TOLUENE-BENZALDEHYDE SYSTEM AT 760 mm.Hg.PRESSURE

Mole fraction of toluene in liquid phase(x_1)	$K_1 (=y_1/x_1)$	$K_2 (y_2/x_2)$	Relative volatility (α)
0.006	.1000	1.0574	.0946
.013	.1300	1.0967	.1185
.019	.1418	1.1328	.1252
.026	.1566	1.1679	.1341
.032	.1649	1.2010	.1373
.045	.1907	1.2500	.1525
.058	.2064	1.3102	.1575
.091	.2500	1.4292	.1749
.124	.2818	1.5643	.1802
.158	.3141	1.6942	.1854
.196	.3519	1.8149	.1939
.242	.3954	1.9536	.2024
.299	.4430	1.1569	.2054
.362	.4993	2.3200	.2152
.445	.5705	2.5227	.2261
.525	.6481	2.5000	.2593
.655	.7443	2.875	.2589
.713	.8011	2.6091	.3071
.772	.8530	2.4000	.3554
.860	.9053	2.8000	.3233
.940	.9741	1.7143	.5682
.980	.9949	1.3333	.7462

CHAPTER 8

THERMODYNAMIC CONSISTENCY

The subject of thermodynamic consistency is important because inaccuracies are often likely to occur in the experimental measurements through human or mechanical errors. If erroneous data go undetected, incorrect conclusions might be drawn about a design or a theory. This obviously makes methods for recognizing and rejecting incorrect vapor-liquid equilibrium data of considerable value. Experimental y/x ratios directly may be tested for thermodynamic consistency or they may be converted to activity coefficients and then tested. The thermodynamic consistency tests are based on well known Gibbs-Duhem equation (31). All constant temperature and pressure, Redlich and Kister (34) developed the following relation:

$$\int_{x_1=0}^{x_1=1} \ln \frac{y_1}{x_1} dx_1 = 0$$

This relation is used to test the consistency of the data. The area under the curve of $\ln \frac{y_1}{x_1}$ vs x_1 from $x_1 = 0$ to $x_1 = 1.0$ should add to zero. This test is mostly applied to data taken at constant temperature. Herrington (34) has shown that the area test for constant pressure system should be

$$\int_{x_1=0}^{x_1=1} \ln \frac{\gamma_1}{\gamma_2} dx_1 = \int_{x_1=0}^{x_1=1} - \frac{H}{RT^2} \left(\frac{dT}{dx_1} \right) dx_1 \quad (42)$$

and a testing method has been devised in the following manner:

For the data to be consistent, $D < J$

where I = net area under $\log \gamma_1 / \gamma_2$ versus x_1 plot and is taken without regard to sign.

Σ = the arithmetic sum of both positive and negative areas under the \log vs x_1 plot.

Θ = maximum temperature difference of the binary system and T_m = minimum boiling temperature in the system.

Thus it is seen that; for consistent data at constant temperature and pressure, the Gibbs Duhem equation takes the form:

$$x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{T,P} + x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_1} \right)_{T,P} = 0 \quad (43)$$

(For a binary mixture)

From this relation; the following conclusions may be drawn for the consistency test (2)

1. Slope Test: For any particular value of x_1 , the above equation should be satisfied. However for isobaric systems, this assumes that effect of temperature on activity coefficient is negligible which is seldom true.

2. Data Fitting Method: As slopes are rather difficult to determine accurately; various forms of integrated Gibbs Duhem equation could be applied to the data. A few of these equations are

1. Vanlaar (4)
2. Margules (4)
3. Wohl (45)
4. Redlich-Kister (33)
5. Wilson (44)
6. Adjusted series expansion of Relative Volatility(10)

This approach suffers from the drawback that the uncertainty as to whether the deviations are due to experimental errors or due to the inadequacy of the equation employed can not be avoided.

3. Area Test: In order to overcome the difficulties mentioned above, (33) Redlich and Kister developed equation (33) which should be satisfied for consistent data. And this assumes the fact that the effect of temperature on activity coefficient is neglected.

4. Test of log - Composition Plots:

Visual Tests (21)

These tests are applicable to binary solutions of non-electrolytes. These tests assume the use of Gibbs-Duhem equation and the consideration of certain strategic compositions on a semi logarithmic plot of activity coefficient γ vs. composition x .

If $\log \gamma_1 = \alpha$ when $x_1 = 0$ (Infinite Dilution)
 and $\log \gamma_2 = \beta$ when $x_2 = 0$ then $\alpha = A$, $2\beta = B$ for Van laar
 equation. Similarly the constants of other models can be
 related to .

The strategic points are selected to be at x_1 (=liquid
 composition) = 0.0; 0.2113, 0.25, 0.50, 0.75, 0.7887 and 1.0.

- a) at $x_1 = 0.5$; $\log \gamma_1 = 0.25 \beta$ and $\log \gamma_2 = 0.25 \alpha$
- b) at $x_1 = 0.25$, $\log \gamma_1 = (\log \gamma_2 \text{ at } x_1 = 0.75)$
- c) If $\alpha = \beta$, $(\log \gamma_1 \text{ at } x_1 = x) = (\log \gamma_2 \text{ at } x_1 = 1-x)$
- d) If $\alpha > \beta$; $(\log \gamma_1 \text{ at } x_1 = 0.5) < (\log \gamma_2 \text{ at } x_1 = 0.5)$
- e) If $\alpha < \beta$; $(\log \gamma_1 \text{ at } x_1 = 0.5) > (\log \gamma_2 \text{ at } x_1 = 0.5)$
- f) $(\log \gamma_1 / \gamma_2) \text{ (at } x_1 = 0.2113)$

$$= \log \gamma_2 / \gamma_1 \text{ at } x_1 = 0.7887$$

- g) Both $\log \gamma$ and curves approach their zero values with a
 horizontal tangency
- h) The two areas bounded by the $\log \gamma$ curves and the $x_1=0$ and
 $x_1=1$ lines should be identical.
- i) If there is no maximum or minimum in the curves, all points
 on both the curves should lie on the same side of the $\log \gamma = 0$
 line.
- j) The plot of $(\log \gamma_1)^{1/2}$ vs $(\log \gamma_2)^{1/2}$ should give a smooth
 line or curve.

When these tests were applied to the Methanol-methylene
 chloride system the results obtained were as follows.

1. Slope Test:

At $x_1 = 0.5$

$$\frac{\partial \ln \gamma_1}{\partial x_1} = -0.167 \quad \text{and} \quad \frac{\partial \ln \gamma_2}{\partial x_1} = 1.5$$

$$\begin{aligned} \therefore x_1 \left(\frac{\partial \ln \gamma_1}{\partial x_1} \right)_{x_1=0.5} + x_2 \left(\frac{\partial \ln \gamma_2}{\partial x_1} \right)_{x_1=0.5} \\ = (0.5 \times -0.167) + (0.5 \times 1.5) \\ = 0.75 - 0.835 = -0.085 (\neq 0) \end{aligned}$$

2. Most of the various models as discussed above were tried for fitting the experimental data. Van laar, Redlich-Kister, 3-suffix Margules and Wilsons models were tried with IBM 7044 computer to fit the data. It was found that none of these models fitted the experimental data and the deviation of the calculation values from the observed values was about 200 percent which clearly indicated the higher non-ideal behavior of the system. However, the fit of the third order \mathcal{A} -equation(10) was exceedingly good. At 550 mm mercury pressure for the methanol-methylenechloride system the values of the constants of this model (Eqn.36) are given in Chapter 7.

3. Area Test:

The plot of $\ln \gamma_1 / \gamma_2$ vs x_1 (Figure 17) shows that the area above the x-axis = ± 0.015 ; area above the y-axis = 0.65

$$\text{Hence } \int_{x_1=0}^1 \ln \gamma_1 / \gamma_2 dx_1 = 0.015 - 0.65 = -0.635$$

$$\text{Hence } \left[\int_{x_1=0}^1 \left(\ln \gamma_1 / \gamma_2 dx_1 \right) \right] \neq 0$$

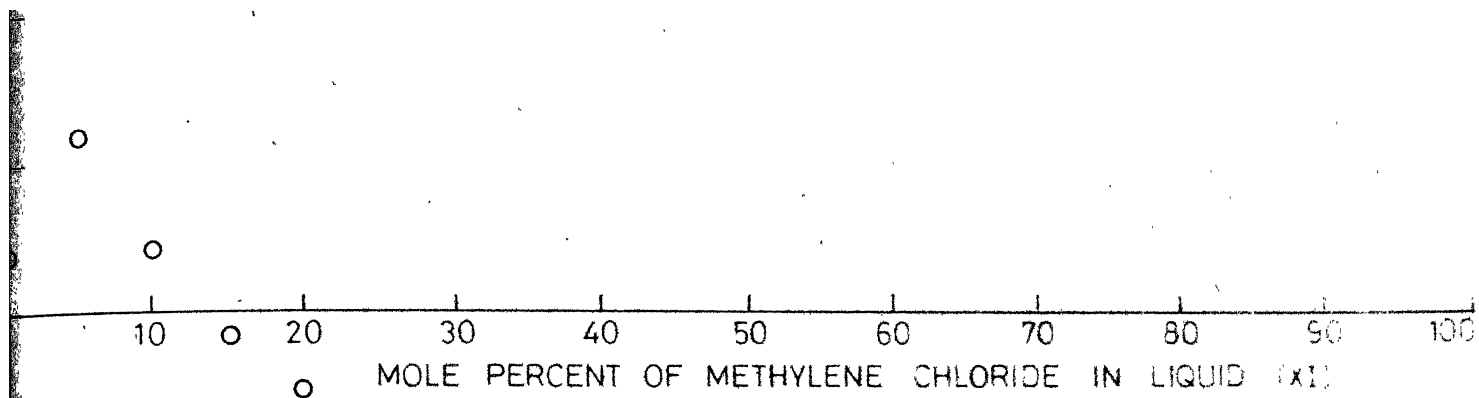


FIG. 17. " $\ln \gamma_1 / \gamma_2$ -MOLE PERCENT METHYLENE CHLORIDE IN LIQUID"
FOR METHANOL METHYLENE CHLORIDE SYSTEM
AT 550 mm. MERCURY PRESSURE.

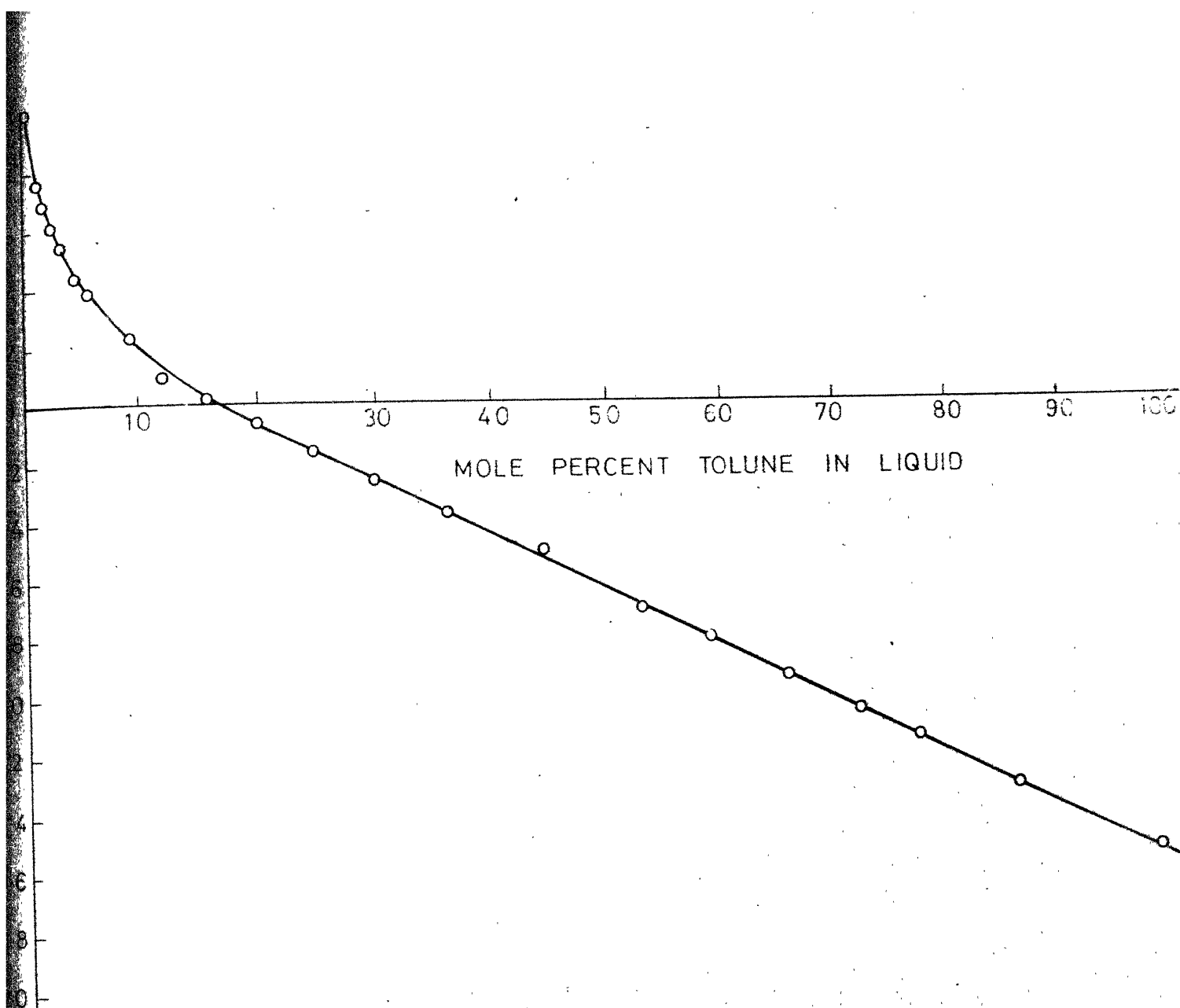


FIG. 18 $\ln p_1/p_2$ COMPOSITION DIAGRAM FOR TOLUENE
BENZALDEHYDE SYSTEM AT 760 MM Hg. PRESSURE

Now $I = 0.635$

$$= 0.015 + 0.65 = 0.665$$

$$= (55.95 - 28.88)^\circ\text{C} = 27.07^\circ\text{C}$$

$$T = 28.88^\circ\text{C}$$

$$D = \frac{I}{\Sigma} \times 100 = \frac{.635}{.665} \times 100 = 95.5$$

and $J = \frac{150 \times \theta}{T_m} = \frac{(150 \times 27.07)}{28.88} = 140.00$

Hence $D < J$

This shows that the data are consistent according to Herrington's (33) test. Applying the tests to the Benzaldehyde-Toluene system the following results were obtained.

The Redlich-Kister area test:

$$\text{Area above the x-axis} = .06$$

$$\text{Area below the axis} = 0.68$$

Hence $\int_{x=0}^1 (y_1 - y_2) dx \neq 0$

Applying Herrington's area test

$$I = .62$$

$$\Sigma = .74$$

$$\theta = (179.04 - 110.62) = 62.39^\circ\text{C}$$

$$T_m = 110.62^\circ\text{C}$$

Hence $D = \frac{I}{\Sigma} \times 100 = \frac{.62}{.74} \times 100 = 67.0\%$

And $J = \frac{150 \times 62.39}{110.62} = 94.0$

Thus $D < J$

This shows that the data are consistent according to the Herrington's area test.

DISCUSSION OF RESULTS

The Methanol-Methylene Chloride System:

The methanol-methylene chloride system forms a low boiling azeotrope at 550 mm.Hg. pressure at 28.88°C and 88.50 mole percent methylene chloride (Figure 9). These data can be compared with the results obtained by Sarma (35) and Tenn and Missen (41) at 760 and 750 mm Hg. pressure respectively. These results indicate clearly that effect of pressure on the azeotrope is considerable.

The activity coefficients, as mentioned in Chapter 6 were calculated taking the vapor phase non-ideality into consideration. It was observed that the fugacity coefficients varied from 0.9718 to 1.0108 and hence should not be neglected in computing the activity coefficients. The activity coefficient of methylene chloride plotted against its liquid phase composition exhibited a maxima at a fairly low concentration range. This abnormal behavior was also observed in the methanol-chloroform, methanol-carbon tetrachloride and methanol-methylene chlorides at 760 mm Hg. pressure systems. This kind of a behavior may be due to high degree of non-ideality of the system which may be attributed to the association between the methanol molecules and a strong dipole-dipole interaction between methanol and methylene chloride molecules. The Van laar, Redlich-Kister, and 3-suffix Margules models were fitted to the y - x data but

could not give satisfactory fit under permissible degree of tolerance between the observed and calculated values. However, the 3rd order, 4 suffix equation (discussed in Chapter 7) fitted the data quite satisfactorily with an average deviation of ± 0.18 in the relative volatility. The data were assessed for thermodynamic consistency (as discussed in Chapter 8) and it was found that the Redlich-Kister, area test failed since the area below the x axis was much more than the area above the axis (Figure 17). This may be due to the unavailability of the excess enthalpy of mixing which the test assumes to be zero.

Toluene-Benzaldehyde System:

For the toluene benzaldehyde system the activity coefficients were calculated taking the vapor phase non-ideality into consideration and it was observed that although the vapor phase fugacity coefficients varied from 0.985 to 1.03, the reference state fugacity coefficient varied from 0.15 to 4.10 atmospheres hence it can not be approximated to the saturated vapor pressure. Since the activity coefficient is a function of temperature, it requires accurate vapor pressure data for its determination. For this system, it was found that, the Antoine equation was not good enough to calculate vapor pressure for toluene since the vapor pressure values of toluene at a dilute toluene concentration range (i.e. at temperatures sufficiently higher than the boiling

point of toluene) was much more than 1500 mm Hg. pressure. Hence the modified Plank-Baehr equation was used to calculate the vapor pressure of toluene. The vapor pressure of benzaldehyde at different temperatures were calculated by Antoine equation, the constants of which were obtained by linear regression analysis of the Stull's experimental data. The data were found to be thermodynamically consistent satisfying the Herrington's area test.

...

CHAPTER 10

SUGGESTIONS FOR FUTURE WORK

Equilibrium Still:

The type of still used in this investigation is exceedingly good to operate at or below atmospheric pressures. But essentially it should be used over a lower working temperature range of the order of 100°C. Beyond this, the entire still surface gets heated up and there is a lot of heat loss due to radiation although it is provided with a vacuum jacket and the surface is silvered. Besides this, the number of slots in the outer contactor surface should be reduced to 5 or 6 from 8 and the slots in the inner surface of the contactor should be reduced to only 1 or 2 at the most from 4 to avoid turbulence and quick fall in level in the contactor due to over bubbling of the vapor from the vaporizer. This will also help in maintaining a calm atmosphere in the contactor resulting in increased residence time of the vapor in the contactor thus improving upon the vapor-liquid contact. Besides, the vaporizer and contactor volumes should be reduced by 5 cc to handle less liquid which thus will eliminate the wastage of costly liquids. The stopcocks used in the line, specially when operated under low pressure should be high vacuum ones (preferably Ace Glass Corporation, Vineland, U.S.A.) to avoid leakage.

Heating Device in the Still:

The heater used for the cell liquid to be heated in the vaporizer should properly designed to allow just the amount of wattage necessary through regulated voltage which should not undergo any fluctuation during operation. To take care of this, a stabilizer should be used. The heater well should be just enough long to heat the surrounding liquid uniformly by the heater and avoid localization of heat due to non-uniform heating which results in bumping of the liquid from the vaporizer to the contactor and vice versa.

LITERATURE CITED

1. Bensen, H.E., Field, J.H., Haynes, W.P., "Chem. Eng. Progr., 52, 433 (1956).
2. Bevmann, R.F.Z., Chem. Ing. Tech., 28, 396 (1956).
3. Burriss, W.L., Reamer, H.H., Sage, B.H., Ind. Eng. Chem., 45, 210 (1953).
4. Carlson, H.C., Colburn, A.P., Ind. Eng. Chem., 34, 581 (1942).
5. Edmister, W.C., Robinson, R.L., Chem. Eng. Progr. Symposium Ser., 59 (44), 11 (1963).
6. Ewell, R.H., Harrison, J.M., Berg, Loyd., Ind. Eng. Chem., 36, 871 (1944).
7. Griswold, J., Wong, S.Y., Chem. Eng. Progr. Symposium Ser., 48 (3), 18 (1952).
8. Hala, E., Coll. Czech. Chem. Commun., 22, 1727 (1957).
9. Hala, E., Pick, J., Fried, V., Volliam, O. "Vapor Liquid Equilibrium", Pergamon Press, Oxford (1967).
10. Hala, E., Wichterle, I., Polak, J., Boublik, T. "Vapor Liquid Equilibrium Data at Normal Pressures", Pergamon Press, Oxford (1968).
11. Herrington, E.E.G., J. Inst. Petrol; 37, 457 (1951).
12. Hipkin, H., Myers, H.S., Ind. Eng. Chem., 46, 2524 (1954).
13. Holmes, J.M., Van Winkle, Mathew, Ind. Eng. Chem., 62(1), 21 (1970).
14. Holland, C.D. "Multicomponent Distillation" Prentice-Hall, Inc., Englewood Cliffs, New Jersey (1963).
15. Jamagvchi, T., J. Tokyo-Chem. Soc., 34, 691 (1913).
16. Jordan, D.G. "Chemical Process Development Part 1"; Inter Science Publishers (1968).
17. Karr, A.E., Scheibel, E.G., Buwes, W.M., Ind. Eng. Chem., 43, 961 (1951).
18. King, M.B., "Phase Equilibrium in Mixtures", Pergamon Press Ltd., (1969).
19. Fortum, G., Freir, H.J., Chem. Ing. Tech., 3, 125 (1953).

20. Kudchadker, A.P., Alani, G.H., Zwolinski, B.J., "The Critical Constants of Organic Substances", Paper No.89; A.P.I. Research Project, 44.
21. Kudchadker, A.P., Eubank, P.T., J.Chem. Eng. Data., 15(1), 7 (1970).
22. Lu, B.C.Y., Can. J. of Chem. Eng., October 3rd, 105 (1960).
23. Lu, B.C.Y., Spinner, I.H., Ho, J.C.K. Can. J. of Chem. Eng., 40, 16(1962).
24. Masia, P., Sonet, M.D.A., Anales Real Soc. Espan, Fis Qim (Madrid), 54(B), 661 (1958).
25. McClellan, A.L., "Tables of Experimental Dipole Moments", W.H. Freeman and Company, San Francisco, 1963.
26. Myers, H.S. Ind. Eng. Chem., 47, 2215 (1955).
27. Orye, R.U., Prausnitz, J.M. Ind. Eng. Chem., 57(5), 18(1965).
28. Othmer, D.F., Ind. Eng. Chem., (Anal. Ed.), 20, 763 (1948).
29. Othmer, D.F., Ind. Eng. Chem., 43, 1607 (1951).
30. Othmer, D.F., Ind. Eng. Chem., 20, 743 (1928).
31. Pitzer, K.S., J. Am. Chem. Soc., 77, 3427, 3433 (1955).
32. Prausnitz, J.M., "Molecular Thermodynamics of Fluid Phase Equilibria", Englewood Cliffs, N.J., Prentice-Hall Inc., (1969).
33. Prausnitz, J.M., Eckert, C.A., Orye, R.V., O'Connell, T.P., "Computer Calculations for Multicomponent Vapor-Liquid Equilibria", Englewood Cliffs, N.J., Prentice Hall, Inc. (1967).
34. Redlich, O., Kister, A.T., Ind. Eng. Chem., 40, 341, 345(1948).
35. Samashima, J., J. Am. Chem. Soc., 40, 1482(1918).
36. Sarma, H., M.Tech. Thesis, I.I.T., Kanpur (1970).
37. Scheller, W.A., Stanley, J.L., J. Chem. Eng. Data, 12(4), 485 (1967).
38. "Selected Values of Properties of Hydrocarbons and related Compounds", American Petroleum Research Project 44, Thermodynamics Research Center, Texas A & M University College Station, Texas (Loose Leaf Data Sheets Extant 1970).

39. Sinor, J., E., Weber, J.H., J.Chem.Eng.Data, 5, 243(1960).
40. Swietoslowsky, W. "Ebulliometric Measurements", (1945).
41. Tenn, F.G., Missen, R.W., Can. J. of Chem. Eng., 41, 13 (1963).
42. Timmermans, J., "Physico Chemical Constants of Pure Organic Compounds" (Vol.I & II) Elsevier Publishing Co., Inc.,(1950,1965).
43. Willey,R.M., Harder,E.H., Ind. Eng. Chem.(Anal Ed), 7, 349 (1938).
44. Williams, F.E., Ind. Eng. Chem., 39, 779 (1947).
45. Wilson, G.M., J.Am.Chem.Soc., 86, 127 (1964).
46. Wohl, K. Trans. Am. Inst. Chem. Engrs., 42, 215 (1946)
47. Yen, L. C. Reed. J. Chem. Eng. Data, 4, 102 (1959).
48. Yen, L.C., Woods, S.S., A.I.Ch.E. Journal, 12 (1), 95(1966).
49. York, R., Ind. Eng. Chem., 34, 345 (1942).
50. Yoshider, F., J. Chem. Eng. Data; 8, 315 (1963).

APPENDIX 1PHYSICAL PROPERTIES (**38**) OF PURE COMPOUNDS

COMPOUNDS	ANTOINE CONSTANTS			P_C (Atm.)	V_C c.c./mole	T_C °K	Z_C
	A	B	C				
METHANOL	7.8975	1474.08	229.13	79.9	118	512.58	0.224
METHYLENE- CHLORIDE	7.0803	1138.91	231.45	60.0	193	510.0	
TOLUENE	6.95464	1344.80	219.482	40.55	322.6	591.72	0.264
BENZALDEHYDE	6.6693	1330.7606	172.8857	21.50	890	625	0.37
BENZENE	6.92679	1222.7583	222.11891				

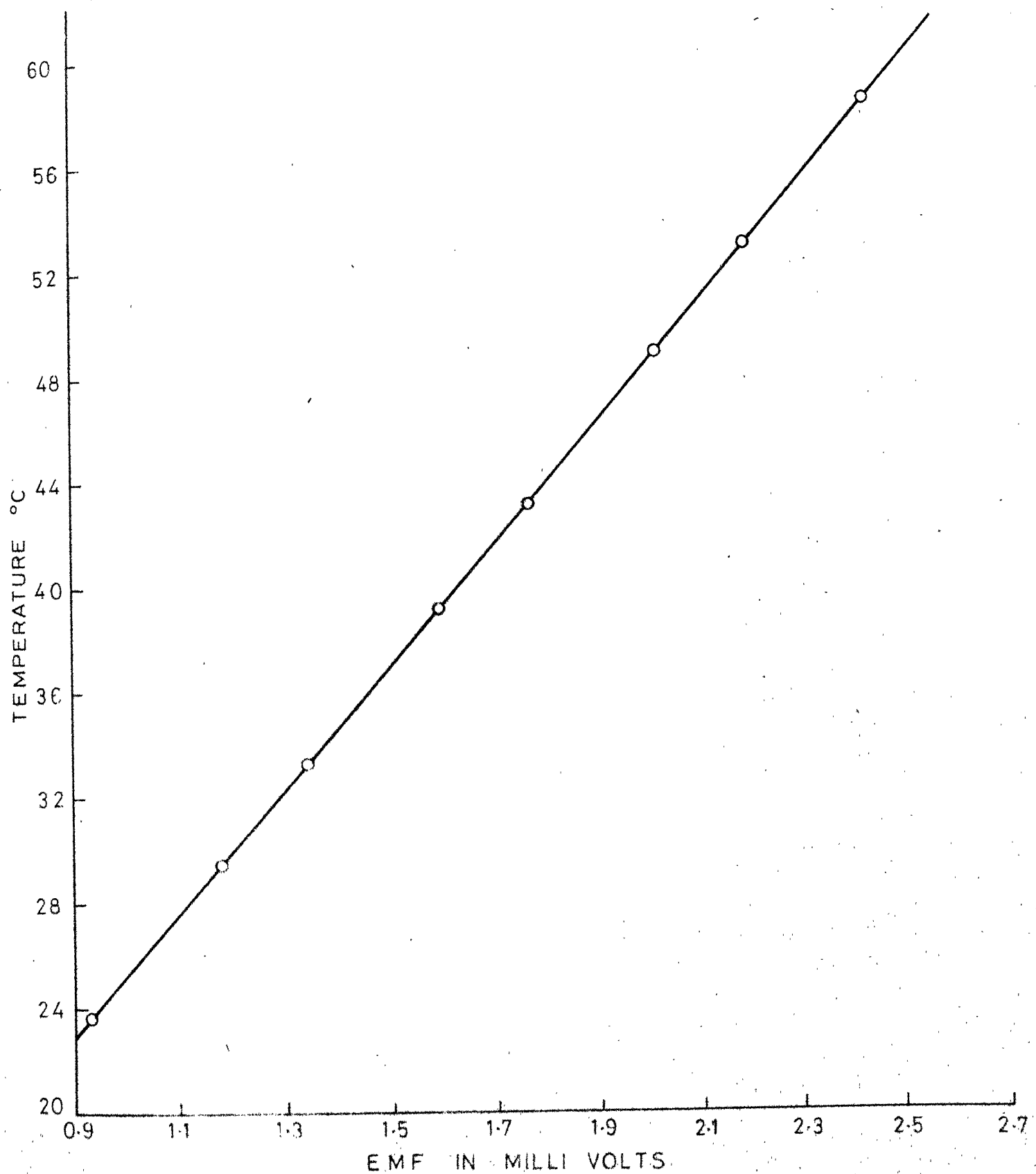


FIG. 7a TEMPERATURE EMF DIAGRAM USED FOR
METHANOL METHYLENE CHLORIDE SYSTEM.

CALIBRATION OF THERMOCOUPLES

THEMOCOUPLE E.M.F. Volts (TC1)	RESISTANCE RATIO	TRUE-TEMP. °C, (T±0.01)
0.00093750	1.0940	23.67
0.00117200	1.1169	29.46
0.00134049	1.1324	33.39
0.00158350	1.1555	39.24
0.00175335	1.1707	43.10
0.00200700	1.1943	49.10
0.00218348	1.2105	53.23
0.00243790	1.2329	58.95
0.00262525	1.2498	63.26
0.00288800	1.2727	69.12
0.00308320	1.2896	73.46
0.00332625	1.3117	79.13
0.00353150	1.3292	83.63
0.00379220	1.3511	89.26
0.00400350	1.3691	93.90
0.00425250	1.3904	99.41
0.00447850	1.4090	104.22
0.00471749	1.4282	109.19
0.00495749	1.4479	114.30
0.00520250	1.4674	119.37
0.00545862	1.4894	125.09
0.00567400	1.5050	129.16

APPENDIX - 3(4)

CALIBRATION OF REFRACTOMETER FOR
Methanol - Methylene Chloride System

Composition of CH_2Cl_2 (Molefraction)	Refractive Index (25 ± 0.01)°C
0.0000	1.3260
0.0649	1.3333
0.1520	1.3423
0.2152	1.3515
0.2960	1.3606
0.3909	1.3700
0.4900	1.3798
0.5976	1.3897
0.7089	1.3994
0.8664	1.4102
1.0000	1.4212

APPENDIX - 3(b)

CALIBRATION OF REFRACTOMETER
(Toluene - benzaldehyde System)

Mole fraction Toluene	λ	Refractive Index (30 \pm 0.01) $^{\circ}$ C
0.0000		1.54078
0.1008		1.53605
0.1458		1.53360
0.200025		1.5314
0.2985		1.5255
0.4513		1.5188
0.625002		1.5115
0.6795		1.50725
0.7606		1.5037
0.8349		1.4996
0.9186		1.49525
1.0000		1.49125

APPENDIX (4) VIRIAL COEFFICIENTS AND MOLAL VOLUMES
OF TOLUENE (1) AND BENZALDEHYDE (2).

$t, ^\circ\text{C}$	B_{11} cc/mole	B_{22} cc/mole	V_{L1} cc/mole	V_{L2} cc/mole
1	2	3	4	5
178.0	-2165.85	-811.09	918.99	273.39
177.0	-2179.04	-815.34	917.78	273.10
176.0	-2192.34	-819.63	916.56	272.82
175.0	-2205.77	-823.95	915.33	272.53
174.0	-2219.32	-828.30	914.09	272.25
173.0	-2232.99	-832.69	912.85	271.96
172.0	-2246.80	-837.12	911.60	271.68
171.0	-2260.72	-841.57	910.33	271.40
170.0	-2274.79	-846.07	909.07	271.11
165.0	-2347.13	-869.09	902.63	269.70
160.0	-2423.03	-893.10	896.04	268.29
155.0	-2502.79	-918.11	889.32	266.88
150.0	-2586.69	-944.23	882.49	265.48
145.0	-2675.09	-971.53	875.57	264.09
140.0	-2768.37	-1000.10	868.58	262.71
135.0	-2866.93	-1030.01	861.55	261.33
130.0	-2971.26	-1061.38	854.48	259.95
125.0	-3081.87	-1094.34	847.39	258.58
120.0	-3199.37	-1128.99	840.31	257.21

TABLE (Continued)

1	2	3	4	5
119.0	-3223.76	-1136.14	838.90	256.94
118.0	-3248.45	-1143.36	837.49	256.67
117.0	-3273.45	-1150.66	836.07	256.40
116.0	-3298.77	-1158.03	834.66	256.13
115.0	-3324.42	-1165.49	833.25	255.86
114.0	-3350.40	-1173.02	831.84	255.58
113.0	-3373.72	-1180.64	830.44	255.31
112.0	-3403.38	-1188.34	829.03	255.04
111.0	-3430.40	-1196.12	827.63	254.77

Acentric Factor for toluene = 0.4907

Acentric Factor for benzaldehyde = 0.2650

APPENDIX 4(b)- VIRIAL-COEFF. AND MOLAR LIQUID VOLUME OF
METHANOL(2) AND METHYLENE CHLORIDE (1) AT THE
REQUIRED TEMPERATURES.

$t, ^\circ\text{C}$	$B_{11}(\text{cc/gmole})$	$B_{22}(\text{cc/gmole})$	$V_{L1}(\text{cc/gmole})$	$V_{L2}(\text{cc/gmole})$
55.95	-660.0	-1050.0	156.750	42.31
54.45	-668.0	-1065.0	156.470	42.23
52.25	-678.0	-1102.0	156.060	42.18
50.70	-690.0	-1155.0	155.771	42.04
49.21	-698.0	-1190.0	155.494	41.96
46.70	-710.0	-1250.0	155.028	41.83
44.58	-720.0	-1310.0	154.635	41.72
42.50	-735.0	-1375.0	154.250	41.61
40.62	-750.0	-1425.0	153.903	41.52
39.00	-765.0	-1480.0	153.604	41.42
37.48	-775.0	-1538.0	153.324	41.34
36.15	-782.0	-1580.0	152.080	41.28
34.95	-794.0	-1630.0	158.859	41.21
33.90	-800.0	-1670.0	152.666	41.18
32.95	-810.0	-1710.0	152.492	41.11
32.05	-815.0	-1740.0	152.327	41.08
31.28	-825.0	-1790.0	152.186	41.03
30.35	-830.0	-1840.0	151.634	40.98
29.60	-840.0	-1880.0	151.897	40.95
29.05	-845.0	-1900.0	151.778	40.92
28.88	-848.0	-1910.0	151.741	40.90
28.90	-847.0	-1905.0	151.750	40.91
29.10	-844.0	-1895.0	151.767	40.93
29.40	-843.0	-1888.0	151.842	40.94
29.95	-838.0	-1878.0	151.942	40.96
30.98	-835.0	-1810.0	152.131	41.00

LIBRARY
5

Date Slip

This book is to be returned
on the date last stamped.

CHE-1971-M-CHH-VAP

.